B-200

FINAL REPORT

RESEARCH GRANT RG-4945

APPLICATION OF GAS CHROMATOGRAPHY TO SLUDGE DIGESTION GAS ANALYSIS

By

WERNER N. GRUNE
Professor of Sanitary Engineering
and
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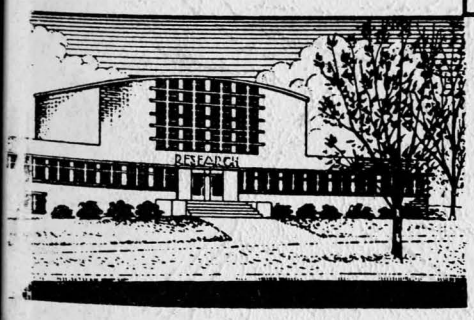
Covering the Period
1 November 1956 to 30 May 1962

Performed for

NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Washington 25, D.C.



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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ABSTRACT

The purpose of these investigations was to develop the gas chromatographic method for the rapid and accurate analysis of the gases of decomposition from anaerobic digestion. The theoretical aspects of gas chromatographic separation are reviewed. Based on the fundamental theory, the specific retention volume, number of theoretical plates, H.E.T.P., and the separation factors are defined. These parameters serve as guides in the selection of optimum gas chromatographic columns.

A gas chromatographic analyzing unit was designed and constructed to meet specific needs for the analysis of gases from sludge digestion. Complete gas analyses from each of 16 digesters could be repeated for any predetermined time interval by means of an automatic sampling valve which was developed specifically for this application.

A major effort of the research program was devoted to the determination of the most suitable column materials for sludge gas analysis. Over fifty different solid and liquid materials were studied and about two hundred columns were prepared and investigated. Among the solid adsorbents studied, it was found that activated charcoal and silica gel were able to separate N_2, CH_4 and CO_2. Molecular sieves 5A and 13X separated H_2, O_2, N_2 and CH_4, but adsorbed CO_2 and H_2S irreversibly. Among the partition liquids studied, tri-m-cresyl phosphate, tetra-isobutylene, squalane, silicone oil 550 and silicone grease were able to separate N_2, CH_4, CO_2 and H_2S. Dimethyl sulfolane was especially suitable for the separation of CO_2 from CH_4; as was Triton X-100 for the separation of H_2S from CH_4 and CO_2. Generally, greater lengths (60 to 80 feet) of liquid partition columns are required than solid adsorption columns (a few inches to 12 feet) to achieve the same

degree of separation. Nevertheless, the liquid partition column is preferred because of the sharpness of peaks produced and the longer column life demonstrated. A 70-ft silicone grease column is considered an optimum column for the analysis of N_2, CH_4, CO_2 and H_2S. However, to separate H_2, O_2 and N_2, a 12-ft molecular sieve solid adsorption column is recommended. With a two-stage columns arrangement, the complete analysis of H_2, O_2, N_2, CH_4, CO_2 and H_2S was accomplished by the combination of a 26-ft Triton X-100 column and a 9-ft molecular sieve, type 5A, column.

The greatest difficulty encountered in the analysis of hydrogen sulfide was the irreversible adsorption of the gas by the column support material. A procedure to de-activate the solid support material is described. Triton X-100 coating on Fluoropak is considered an optimum partition column combination for the separation of H_2S from the other sludge digestion gas components.

The analysis procedure, beginning with the gas sampling to the interpretation of chromatograms, is described in detail. The "peak height fraction" method is suggested for the interpretation of chromatograms. This method eliminates the necessity of calibration curves for the individual components.

The relation of the CO_2 concentration to the progress of digestion was observed by the daily analysis of the gases produced from 16 laboratory digesters. The analyses were performed during 24 experimental digestion studies, ranging from 40 to 90 days each. The initial CO_2 concentration of the sludge gas was generally found to be 60% (by volume) or higher, but dropped to 20 to 30% after five or six days of digestion if the process proceeded in the normal manner. A CO_2 concentration in excess of 30% in sludge gas, after ten days of digestion, definitely indicated that unfavorable conditions were upsetting the normal digestion process.

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GLOSSARY

Adsorption column (or gas-solid adsorption column): A column packed by a solid adsorbent, such as activated charcoal.

Apparent retention time: The difference of the retention time of a solute and the retention time of an inert gas.

Apparent retention volume: The product of apparent retention time and flow rate.

Carrier gas: A continuous gas flow which brings the sample gas through a chromatographic column.

Chromatogram: A plot of concentration (or its equivalent, such as millivolt from a thermal conductivity cell) of a particular solute in the effluent emerging from a column versus elution time.

Column (or gas chromatographic column): A column uniformly packed with a solid adsorbent or inert solid coated with a liquid, used to separate the components from a gas mixture.

Flow rate: The volumetric rate of carrier gas passing through a column, measured at the temperature and pressure at the exit of the column.

Height equivalent to a theoretical plate: Length of chromatographic column divided by the number of theoretical plates.

Inert gas: Gas which is not retained by the solid adsorbent or partition liquid of a chromatographic column.

Irreversible adsorption: The adsorption power of the adsorbent in the column is so strong that the solute cannot be eluted by the carrier gas in a reasonable period.

Number of theoretical plates (n,N): Number of equivalent theoretical plates of a column.

Partition column (or gas-liquid partition column): A column packed with an inert solid, such as C-22 firebrick, which has been coated with an organic liquid such as silicone grease.

Partition liquid: An organic liquid which is used as a coating material in a gas-liquid partition column.

Peak height: The maximum height of a chromatogram, or maximum ordinate of a peak.

Peak width (w): The distance between the intersections of the two tangents with the horizontal (time) axis. The tangents are drawn on the inflection points of a chromatogram.

Plates per foot of column length: Number of theoretical plates divided by the length of the column.

Retention time (d): The time interval between the injection of a sample and its appearance as the maximum ordinate of the peak.

GLOSSARY

Continued

Retention volume: The product of retention time and flow rate.

Separation factor: A measurement of the degree of separation between two peaks.

Sensitivity index: A measurement of the sensitivity of a sample detector.

Specific retention volume (V_g^o): Retention volume divided by the total weight of partition liquid or solid adsorbent inside the column.

Stationary phase: Partition liquid (or solid adsorbent) plus the solute which dissolved (or adsorbed)in it.

Theoretical plates: A discrete stage in which the equilibrium is established between the two phases before these two phases are separated.

Chapter 1

INTRODUCTION

Purpose

It has been generally established that sludge digestion gas is composed of approximately 60 to 65 percent methane, 25 to 35 percent carbon dioxide, and that the remainder may be comprised of trace quantities of nitrogen, hydrogen, ammonia and oxygen, depending on the state of the digestion process. To determine the qualitative and quantitative analysis of sludge digestion gas, the studies reported herein were performed. As a result of these studies a precise analytical method to assist the operation of anaerobic digestion has been developed. The need for a rapid and precise analysis of sludge digestion gas composition arises from a number of considerations such as (a) the concentration of methane to indicate the calorific value, (b) the concentration of carbon dioxide to reflect how well digestion is proceeding, (c) the concentration of hydrogen sulfide to show if gas scrubbing is needed to prevent corrosion of engines if the sludge gas is utilized, and other purposes. Therefore, it was decided to develop a procedure for the simultaneous quantitative and qualitative determination of the gases of decomposition from sludge digestion.

Significance

The literature (1) distinguishes three stages of digestion: (a) intensive acid production as the initial stage; (b) followed by acid regression as the second stage; and (c) intensive digestion of the more resistant materials as the final or alkaline fermentation stage. As digestion proceeds through these stages, the total cumulative gas production per gram of volatile matter destroyed increases. It is generally known that during the first stage of

digestion, carbohydrates and simple organics are attacked, resulting in a predominant production of carbon dioxide during this initial period. The methane production gradually increases, especially during the second stage, and then levels out in the third stage to approach ultimately the asymptotic value of about 75 percent CH_4 and 25 percent CO_2 for well digested, domestic sewage sludge. In most plants, the digestion process is not allowed to go to completion (90 percent of the total gas yield or more) because of digester capacity and therefore the process operates short of the ultimate values given above, but perhaps closer to 60 to 65 percent CH_4 as stated earlier. However, the literature is devoid of details or information correlating the progress of digestion with the quality of sludge gas produced.

Babbitt (2) was cognizant of the importance of gas production when he stated that the quantity and quality of gas produced are probably the best indices of the progress of digestion. He also pointed out the need for H_2S scrubbing to protect the gas engine against corrosion when sludge gas is utilized.

More recently, Miller and Barron (3) reported that based on their experiences "the carbon dioxide in digester gas above the established normal is the best early warning signal of failure yet discovered and usually becomes evident in time to take corrective measures."

A number of other investigators (4)(5) have been interested in studying the relationship of H_2S production during anaerobic digestion of sewage sludge for a number of reasons, one of which has been to establish the role played by this polar gas. Although no definite relationship has been established, it appears that H_2S may be a significant indicator of the properties and organics of the sludge.

Because of the many problems encountered in plant operation and in research laboratories, a simple, precise method of gas analysis has wide application in waste treatment process operation. If the operator is able to have a few hours warning, as indicated by the onset of an increased CO_2 concentration, many digestion difficulties can be avoided. Beyond the need for measuring the CH_4 and CO_2 concentrations in sludge gas to analyze the effectiveness of plant operation, it is also necessary to analyze for nitrogen to determine if the method of sludge digestion gas sampling is under control, which can only be achieved if sampling is conducted carefully. The analysis of CO_2 by Hempel or Orsat using NaOH or KOH absorption burets only is subject to considerable error for routine plant analysis. There is no assurance that the sample introduced is 100 per cent sludge digestion gas, as it may contain air which was introduced during sampling. Therefore, the interference-free gas chromatographic method of analysis is of greatest advantage in this area.

Although gas chromatography was rarely used prior to 1956, during the past five years gas chromatography has matured to a fully grown branch of instrumental analysis. The method is now accepted by many research laboratories and process industries as one of the standard procedures for the analysis of gases and organic compounds. However, gas chromatography has been slow to find its way into the fields of sanitary chemistry and environmental engineering. Among the great variety of gas chromatographic analyzers now available on the market, none are specifically designed for the analysis of sludge gas. The selection of a suitable unit, and probably more important, the need to devise a suitable chromatographic column, has often discouraged a novice to the field of gas chromatography.

Scope of Work

The results of five years of research are reported herein. The results covered in this report span the period from 1 December, 1956 to 15 April, 1962. As part of this study, a suitable apparatus was designed for the specific purpose of analyzing the usual components of sludge digestion gas. After many modifications to improve the sensitivity, the apparatus was constructed in the laboratory, employing gas-solid adsorption columns or gas-liquid partition columns. Both types of columns were studied under a variety of operating conditions and compared for efficiency and optimum separation of components found in sludge digestion gas. As pointed out in Chapter 2, all studies to evaluate and compare columns under various operating conditions were based on specific retention volumes and separation factors. Final selection of the column, or multiple columns, was based on several criteria: (a) greatest number of components resolved, (b) maximum sharpness of peak achieved, (c) optimum column life attainable, (d) ease of interpretation of chromatogram, and (e) operating conditions which are readily available.

Resolution of CH_4, CO_2, H_2S, N_2, H_2, NH_3 and O_2, was strived for as these gases are present in sludge digesters, ranging from large to very small concentrations. The presence of N_2 and O_2 is peculiar perhaps only to laboratory scale research because during the manipulation of the sludge and sampling from small containers, the introduction of air cannot be absolutely avoided.

Results of daily gas analysis by the gas chromatographic method over a period of three years indicate that the progress of sludge digestion could be followed closely by detectable changes in the quality of the gases of decomposition produced during the process.

Throughout these studies a serious attempt was made to simplify the analytical procedure to make it available for routine analysis by plant personnel. The ultimate objectives of the study in this regard were successful, as will be seen from the results reported in the body of the discussion that follows.

Chapter 2

CONCEPTS AND THEORY OF GAS CHROMATOGRAPHY

A. Brief Review of the Development of Gas Chromatography

Chromatographic methods are not new. Chromatography was first employed by Tswett (6) in 1906 for separating components of plant pigments by moving the liquid phase over a solid adsorbing agent by the elution method. He obtained discrete bands of colored materials and named this method "chromatography", which literally means "color writing." Although this name has become a misnomer with the application of the more modern methods employing colorless materials, the term is now firmly established and appears to be irreplaceable.

Tswett's technique remained unnoticed for about 25 years only to be rediscovered in almost the same form by Kuhn, Winterstein and Lederer (7), who used a paper chromatographic technique to resolve plant carotene into its components.

The adaptation of adsorption chromatography to mixtures in the form of a gas or vapor (gas-solid chromatography) was due to Turner (8), Claesson (9), James and Phillips (10)(11), but the application of "elution development" [1] has been relatively recent and the development has been generally credited to Cremer (14), Janak (15)(16) and Patton, Lewis and Kaye (17) between 1951 and 1955.

The liquid stationary phase, or the use of "partition" chromatography, was first introduced by Martin and Synge (18) in 1941. Their work also included

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[1] Chromatographic methods may be further classified as to the technique of removing the separated sample components from the column. This technique is usually referred to as "development". Subdivisions according to development include: elution analysis, frontal analysis and displacement analysis. A description of these techniques is beyond the scope of this report but may be found in other publications (12)(13). In the research performed in this report, the elution development technique was used exclusively.

using a liquid moving phase. In spite of the advantages suggested by these authors to employ a gaseous mobile phase with a similar liquid-coated stationary phase, it remained for James and Martin (19)(20) to present the results of the first such application in 1952. In short succession, others followed to take advantage of the gas-liquid chromatography method; Ray (21), Griffiths and Phillips (22) in 1954, Bradford, Harvey and Chalkley (23) in 1955. The discovery of the capillary column by Golay (24) in 1958 opened yet an entirely new branch of gas-liquid partition chromatography.

B. Fundamental Principles

The following definition embodies a common feature present in the execution of all chromatographic separations, according to Keulemans (12):

> "Chromatography is a physico-chemical method of separation in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or is temporarily adsorbed by the solid bed."

The extent to which adsorption plays a role varies greatly depending on the physical and chemical characteristics of both stationary and moving phases. Resolution and identification of individual components from a mixture is dependent on the effective separation of some or all of the components into concentration zones or "bands" owing to the selective retardation (or "temporary" adsorption) exerted by the stationary phase in equilibrium with the moving phase. Because of the phase equilibrium differences, the sample components will tend to become separated by repeated distribution between the stationary and moving phases as they are moved down the length of a chromatographic column. The phase equilibria for different components of the sample will differ. To illustrate, there will be a difference in the intensity of the force by which the

stationary phase tends to hold each of the sample components, whether the nature of this force be adsorption, solubility, chemical bonding, or molecular filtration.

The basic principles of gas chromatography are not different from those that guide classic liquid chromatography. All types of chromatographic separations involve the transport of a small sample of a liquid or gas (vapor) mixture through a column.

The chromatographic column contains a substance which consists of either a solid adsorbent or a liquid partitioning agent. In the latter, a liquid stationary phase is distributed over an inert solid support to provide a large exchange surface. These two alternatives constitute the stationary phase. The constituents of the sample are transported through the column by means of a gas which constitutes the moving phase. In a properly selected column the stationary phase selectively retards the components of the mixture and causes their movement through the column at different effective rates. During the travel through the column, the components tend to become segregated into separate zones, or "bands" which are detected qualitatively and measured quantitatively by a suitable detecting device at the exit from the column.

C. Theory of Separation; Retention Volume and Peak Width

The principle of chromatographic separation may be briefly explained by the following simplified illustration:

A gas sample contains two components, A and B, that are distributed uniformly in the mobile phase formed by the carrier gas. The carrier gas forces the sample gas through the column which is packed with liquid or solid adsorbent (the stationary phase). Intimate contact between the sample gas and the stationary adsorbent is achieved and as a result the sample gas will distribute itself between the stationary and mobile phases. Suppose now that for component A,

the fraction of X_a is adsorbed in the stationary phase which will leave the quantity $1 - X_a$ in the gas phase. This adsorption means that the probability for each single molecule of component A to stay in the gas phase and to continue moving is $1 - X_a$. As a result, during a definite time interval, component A will move along with the mobile phase only during a fraction $1 - X_a$ of the total time. From similar reasoning, component B will move along with the carrier gas only during a fraction of $1 - X_b$ of the time. If X_a is smaller than X_b, then component A will come out earlier than B, or component A has been separated from component B.

For the convenience of mathematical treatment, it is assumed that the column is formed by a large number of theoretical plates. The plate has the usual meaning as that in a distillation or extraction column[2]. The theoretical plates are assumed as "ideal", i.e., the solute distributed between two phases will reach equilibrium before it moves to another plate. This equilibrium may be expressed by the following equation:

$$y_n = k\, x_n \qquad (1)$$

where:

x_n = the mole fraction of the solute in the stationary phase in plate n,

y_n = the mole fraction of the solute in the mobile phase in plate n,

k = the vapor-liquid equilibrium constant of the solute.

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[2] A continuous countercurrent process, such as distillation and extraction may in theory and sometimes in practice be carried out in a number of discrete plates, each constituting an elementary process in which perfect equilibrium is established between the two phases and in which these phases are then again separated. Such a plate is known as a theoretical plate.

A differential amount, dm_{n-1} mole of carrier gas transfers from plate n-1 to plate n, and carries with it the amount $x_{n-1}dm_{n-1}$ of the solute, while a dm_n mole of gas carries the amount $x_n dm_n$ of the solute from plate n into plate n+1. An overall material balance and solute balance around plate n yields:

$$dm_{n-1} - dm_n = dG_n + dS_n \tag{2}$$

and

$$y_{n-1}dm_{n-1} - y_n dm_n = d(y_n G_n) + d(x_n S_n) \tag{3}$$

where G_n is the mole of gaseous phase and S_n is the mole of stationary phase (including any temporarily adsorbed solute) in the plate n, respectively.

Combining equations (2) and (3) to eliminate dm_{n-1}:

$$(y_{n-1} - y_n)dm_n = (y_n - y_{n-1})dG_n + (x_n - y_{n-1})dS_n + G_n dy_n + S_n dx_n \tag{4}$$

Since:

$$S_n = \frac{M_s}{1 - x_n} \tag{5}$$

where M_s represents the moles of partition liquid or solid adsorbent in each plate, therefore:

$$dS_n = \frac{M_s dx_n}{(1 - x_n)^2}$$

$$= \frac{S_n dx_n}{1 - x_n} \tag{6}$$

Combining equations (1), (4) and (6):

$$(y_{n-1} - y_n)dm_n = (y_n - y_{n-1})dG_n + \frac{S_n(\frac{y_n}{k} - y_{n-1})}{k(1 - x_n)} dy_n + (\frac{S_n}{k} + G_n)dy_n \tag{7}$$

When the sample injected is small, the concentration of the solute in the column, y_n, as well as y_{n-1}, is small; therefore, the first two terms on the right side of the equation (7) are negligible in comparison to the third term. Thus, equation (7) may be simplified to:

$$(y_{n-1} - y_n)dm = (\frac{S}{k} + G)dy_n$$

or

$$\frac{dy_n}{dm} = \frac{y_{n-1} - y_n}{S/k + G} \tag{8}$$

The subscript n on M, S and G in equation (8) is dropped out because all these quantities are the same from plate to plate when the size of sample injected is small.

The above derivation, which is slightly modified from the conventional plate theory as summarized by Keulemans (25), serves to emphasize that equation (8) is valid only when the concentration of solute in the carrier gas is small. These conditions may not be met when large size samples are injected, or when the carrier gas contains considerable amounts of solute prior to the injection of the sample.

If we now define:

$$u = \frac{m}{G + S/k} \tag{9}$$

equation (8) may be simplified to:

$$\frac{dy_n}{du} = y_{n-1} - y_n \tag{10}$$

Equation (10) can be solved by the following procedure with the

initial condition when $m = 0$, $u = 0$, $y = 0$, for all the plates except at the first plate

$$y_o = Y \tag{11}$$

where Y = total solute initially injected.

Starting with the first plate, $n = 0$ and because the inlet flow is solute-free pure helium, we obtain therefore, $y_{n-1} = 0$. Thus, equation (10) becomes:

$$\frac{dy_o}{du} = - y_o \tag{12}$$

The solution of equation (12) with the initial condition of $u = 0$, $y_o = Y$ is:

$$y_o = Ye^{-u} \tag{13}$$

Now let us consider the second plate, $n = 1$, from equation (10):

$$\frac{dy_1}{du} = y_o - y_1 \tag{14}$$

Combining equations (13) and (14):

$$\frac{dy_1}{du} = Ye^{-u} - y_1 \tag{15}$$

Equation (15) is a first order linear equation. Its solution is:

$$y_1 = Yue^{-u} + Ce^{-u} \tag{16}$$

At $u = 0$, $y_1 = 0$, therefore, $C = 0$:

$$y_1 = Yue^{-u} \tag{17}$$

For the third plate, n = 2, equation (10) becomes:

$$\frac{dy_2}{du} = y_1 - y_2 \tag{18}$$

Combining equations (17) and (18):

$$\frac{dy_2}{du} = Yue^{-u} - y_2 \tag{19}$$

Solve equation (19) in the same manner as in the solving of equation (15)

$$y_2 = Y\frac{u^2}{2} e^{-u} \tag{20}$$

By continuing to solve "step by step", it can easily be shown the solution of the above differential equation is:

$$y_n = Y\frac{u^n}{n!} e^{-u} \tag{21}$$

where Y = the initial concentration of solute in the gaseous phase entering the first plate.

If we plot $\frac{y_n}{Y}$ vs. u, a Poisson type curve, which will be very close to a Gaussian type curve, if n is sufficiently large, is obtained.

In order to find the number of moles of the carrier gas which has passed through plate n when the maximum concentration occurs at the plate, let $\frac{dy_n}{dm} = 0$.

From equation (8), when $\frac{dy_n}{dm} = 0$

$$y_n = y_{n-1} \tag{22}$$

Equations (21) and (22) are combined to obtain:

$$\frac{u^n}{n!} = \frac{u^{n-1}}{(n-1)!} \tag{23}$$

or $u = n$ when y_n is maximum.

Equation (23) shows that the maximum concentration occurs at the plate n when u is equal to n.

Substituting n for u into equation (9), we obtain when y_n is maximum:

$$(m)_{max} = n(G + S/k) \tag{24}$$

Consequently, at exit of a column which contains (n + 1) theoretical plates (the plates are numbered as 0, 1, 2 ---n, therefore, for a column which contains (n + 1) plates, the last plate is the nth plate) the concentration of solute will have a maximum value when n(G + S/k) moles of carrier gas have passed through the column.

For large volume of n (say, n > 100)

$$n \doteq n + 1$$

Therefore

$$nG \doteq (n + 1)\, G = \overline{G} \tag{25}$$

$$nS \doteq (n + 1)\, S = \overline{S} \tag{26}$$

where $\overline{G}$ and $\overline{S}$ are the number of moles of the gaseous phase and the stationary phase of the entire column, respectively.

By substituting equations (25) and (26) into equation (24), the following equation is obtained:

$$(m)_{max} = \overline{G} + \overline{S}/k \tag{27}$$

Equation (27) may be changed from the mole basis to volume basis by substituting:

$\rho_G V_N$ for $(m)_{max}$, $\rho_G \overline{V}_G$ for $\overline{G}$, $\rho_S \overline{V}_S$ for $\overline{S}$, and

K for $\dfrac{\rho_S}{k \rho_G}$, from which we may obtain:

$$V_N = \overline{V}_G + K\,\overline{V}_S \tag{28}$$

or

$$V_N - \overline{V}_G = K\,\overline{V}_S \tag{28a}$$

where V_N is defined as the retention volume, ρ_G and ρ_S are the densities of the gaseous phase and stationary phase, respectively, expressed as moles per unit volume, $\overline{V}_G$ and $\overline{V}_S$ are the volume of gas phase and volume of stationary phase inside the whole column, and K is the partition coefficient. From equation (28) we can see that the retention volume, V_N, depends only on K, the partition coefficient, and the volume of vapor and liquid present in the column. Thus, V_N is independent of n, or the number of "theoretical plates" in the column.

$(V_N - \overline{V}_G)$ is defined as the "apparent retention volume". Experimentally it may be obtained according to equation (29):

$$V_N - \overline{V}_G = (\theta - \theta_i)\, C_1\, f_c \tag{29}$$

where

θ = the retention time of the solute, and

θ_i = the retention time of an inert gas which is injected simultaneously with the solute. The inert gas is a gas which does not dissolve in the partition liquid (or solid adsorbent) of the column to any appreciable degree. Air, nitrogen and hydrogen are inert to most columns, whereas, only hydrogen is considered as inert in molecular sieve columns. C_1 is the volumetric flow rate of the carrier gas measured at the column temperature and column exit pressure. f_c is a correction factor, derived by James and Martin (20) to correct for the effect of the pressure gradient across the column, and defined as:

$$f_c = \left(\frac{3}{2}\right) \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \tag{30}$$

where p_i and p_o are the pressures at the column inlet and exit, respectively.

Equation (28) may be rearranged to

$$(V_N - \overline{V}_G)\,\rho = K\,\overline{V}_S\,\rho = K\,W \qquad (31)$$

$$\frac{V_N - \overline{V}_G}{W} = V_g^{\,o} = K/\rho \qquad (32)$$

where ρ = density of stationary phase, gm/ml

W = total weight of stationary phase, gm

$V_g^{\,o}$ = specific retention volume, ml.

Since K and ρ are functions of temperature only for a particular system of gas sample and stationary phase, $V_g^{\,o}$, or the specific retention volume, becomes a convenient parameter to indicate the "retention ability" of the stationary phase.

The specific retention volume, $V_g^{\,o}$, which corresponds to the R_f-value[3] in liquid-liquid column chromatography, expresses the difference between the rate of movement of the carrier gas, or shows the retention power of the stationary phase inside a column. The greater the values of $V_g^{\,o}$, the greater the separation between the peak of an inert gas (such as hydrogen or air) and the particular sample peak. The greater the difference in the specific retention volume between two specific components, the greater will be the separation between peaks of the two components.

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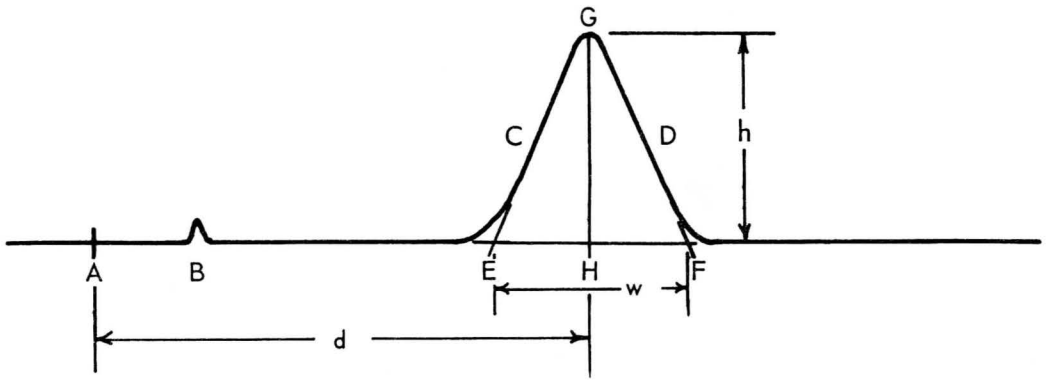
[3] In dealing with liquid-liquid partition, Consden, Gordon & Martin (26) introduced the retardation factor, R_f, to denote the transport ratio between the rate of movement of a volatile solute and the rate of movement of the carrier solvent:

$$R_f = \frac{\text{rate of movement of the solute}}{\text{rate of movement of the fluid}}$$

Obviously, the smaller the value of R_f, the greater the interaction between solute and partition liquid.

After obtaining the second derivative of y_n from equation (21) with respect to u, and setting $d^2y_n/du^2 = 0$, two inflection points at $u = n - \sqrt{n}$ and $u = n + \sqrt{n}$ are found. The tangents at the two inflection points intersect the horizontal axis at $u = n + 1 \pm 2\sqrt{n}$. Therefore, the distance between these two points will be $4\sqrt{n}$, which is defined as peak width, w ($\overline{EF}$ in Figure 1). This parameter, depending on column characteristics and operating conditions, is independent of solute concentration.

If we designate the distance along the u-axis between the injection point and the peak ($\overline{AH}$ in Figure 1) by d, then according to equation (23), $d = n$. Since $d = n$, and $w = 4\sqrt{n}$, it follows that $n = (4\ d/w)^2$. Therefore, the number of equivalent ideal plates of a column may be calculated simply by measuring the retention time and peak width of a gas component. The following assumptions were made to derive the above relationships: (1) K is a constant, independent of solute concentration in the two phases, i.e., a linear distribution isotherm; (2) V_G and V_S, the volume in the gaseous and stationary phases per unit plate, are the same for every plate which means that there is no change of gas density and uniformity of coating throughout the column; and (3) at the beginning, only solute is present in the first plate. The third assumption requires that the sample size is small enough to occupy only the space equivalent to the first plate in a column during sample injection. Experimental results have proven that the retention volume and peak width are practically independent of sample size, provided the sample size is less than five mls.



A = Point of injection
B = Peak of a gaseous component which is not absorbed by a liquid-partition column, or adsorbed by a solid absorption column
C,D = Inflection points
E,F = Intersection of the tangent lines (which are drawn through the inflection points) with the base line
G,H = Chromatographic peak of a solute sample and its projection on base line, respectively
$\overline{AH}$ = d = retention time
$\overline{EF}$ = w = peak width
$\overline{GH}$ = h = peak height

GAS CHROMATOGRAM

Figure 1.

D. Plate Efficiency and Separation Factor

Although many papers have been published describing various means to increase the efficiency of a gas chromatographic column (27)(28)(29)(30) as yet no generally accepted parameter has been established to express quantitatively the efficiency of a column in the separation of two component gases. The term "Number of Theoretical Plates", or its reciprocal value times the column length, "H.E.T.P." (height equivalent to a theoretical plate) is the parameter most frequently appearing in the literature. As discussed on page 17 in the previous chapter, the number of theoretical plates may be calculated from the following expressions:

$$n = (4\frac{d}{w})^2 \qquad (33)$$

and by definition

$$H.E.T.P. = \frac{L}{n} \qquad (34)$$

where n = number of theoretical plates

d = retention distance (distance $\overline{AH}$ in Figure 1)

w = peak width (distance $\overline{EF}$ in Figure 1)

L = length of column.

For the same column, a decrease of the H.E.T.P. value caused by varying any of the operating conditions of the column (temperature, flow rate, etc.) indicates an increase in the efficiency of separation. However, comparison of the efficiency of the separation of two different columns by only correlating their H.E.T.P. values may be greatly misleading. For example, a 71-ft silicone grease-coated partition column, which does not separate nitrogen from oxygen in an air sample, was found to have a theoretical plate number of 2860 for air, or H.E.T.P. of 0.0248 ft. On the other hand, a 12-ft molecular sieve column, which completely separates oxygen from nitrogen in air, possesses merely 275 theoretical

plates for oxygen and 513 theoretical plates for nitrogen, or H.E.T.P. values of 0.032 ft and 0.023 ft, respectively. Therefore, in this particular case, with two columns of approximately the same H.E.T.P. values, a shorter column gave much better separation. The inadequacy of H.E.T.P. as a parameter to indicate the column efficiency has been discussed by Golay (31), Purnell (32), Johnson and Stross (33) in considerable detail. The defect originates from two sources:

(a) In their derivation for the "theoretical plate" theory, Martin and Synge (18) assume that the entire gas sample is injected into the "first plate", in other words, into the very beginning of a column. In practice, there is always a certain "dead" space between the injection point and the start of the column, as well as that between the far end of the column and the detector. Therefore, the "retention distance", d, shown in Figure 1 includes the time required for the sample to traverse the "dead" space, in addition to the traveling time inside the column.

(b) According to the "theoretical plate" theory, the number of the theoretical plates for an inert gas which is not absorbed by the column material should be unity. Experimental evidence does not support the theory since a value of 2860 theoretical plates has been obtained for an air sample passing through a 71-ft silicone grease column which shows little adsorptivity toward air.

Another difficulty encountered when using the number of theoretical plates, or H.E.T.P., as the efficiency parameter is the problem to obtain accurate values. The determination of peak width, w, is generally one source of error. It is difficult to determine the inflection points on a gas chromatogram, and yet, the tangent lines must be drawn at the inflection points. A slight error in determining w will cause considerable error in the number of the ideal plates, since n is inversely proportional to the square of w.

Another parameter, called the Separation Factor, was found to be a better parameter to indicate the separation ability of a column. The separation factor R is defined by the following formula, according to its original definition by Jones and Kieselbach (34), with a slight modification of using average peak width of components 1 and 2 instead of peak width of component 2:

$$R_{1,2} = \frac{2(d_2 - d_1)}{w_1 + w_2} \qquad (35)$$

Quantities d and w have the same meaning as that used in equation (31). Subscripts 1 and 2 refer to components 1 and 2 and $R_{1,2}$ is the separation factor between component 1 and component 2 for a particular column under specified operating conditions.

Theoretically, $R_{1,2} = 1$ is the minimum value required for a complete separation between the two components. In practice, because of the tailing effect, $R_{1,2} > 1.5$ is generally necessary to obtain a satisfactory separation between peaks.

The separation factor has proven to be a reliable parameter to indicate the efficiency of a column in the separation between two components. However, it should be pointed out that an observed increase of the separation between two peaks is not necessarily an advantage for the purpose of analysis. If the distance between two peaks is greater than that required it will merely prolong the analysis time. In the analysis of sludge gas, separations between N_2 [4] and CO_2, and CH_4 and CO_2 are generally achieved easier than separations between N_2 and CH_4. Consequently, the separation factor of the latter mixture

---

[4] Nitrogen, or the mixture of nitrogen and oxygen, is not one of the decomposition products of the sludge digestion process. However, nitrogen was often present in the sludge gas. The gas may come from any air dissolved in the influent, or may leak into the digester from the atmosphere, or be introduced into a sample due to poor sampling technique. It is important to separate it from methane in order to obtain the accurate analysis result.

was usually considered a criterion in the evaluation of a column in this study. The object was to find the column which gave a maximum separation factor for N_2 and CH_4 mixtures under favorable operating conditions without unduly prolonging the separation of N_2 and CO_2.

Chapter 3

LABORATORY EQUIPMENT AND APPARATUS

The basic gas chromatographic analysis system consists of a gas chromatographic column to separate the sample of the gaseous mixture into its component gases, a detector to indicate the amount of each component gas present, and a recorder to record the signal delivered by the detector. The gas chromatographic column (gas-solid adsorption column or gas-liquid partition column) is in general housed in a thermostatic oven which is maintained at a constant or programmed temperature. The detector may be a thermal conductivity cell (filament type or thermistor type) or an ionization detector (hydrogen or argon ray). In some commercial models both types of detector are employed. The recorder in general is a strip-chart, null-point voltage recorder with 0 to 1 millivoltage or 0 to 10 millivoltage full span. It should have a short time constant (two seconds or better).

Accessories may include such items as flash heater to vaporize liquid sample, special injection device, or sample collectors, etc.

A. Special Requirements for a Sludge Gas Analyzer

While there are many different types of gas chromatographic analyzers on the market they must serve a variety of analytical needs, ranging from determinations of high boiling point liquids to permanent gases. Not all gas chromatographic units are suitable for the analysis of sludge digestion gas, both in respect of first cost and sensitivity of detection. Most types of commercial gas chromatography units incorporate one or more of the following features which are unnecessary or useless for the analysis of sludge digestion gas components:

(1) Ionization detector: Both the hydrogen flame and the argon beta-ray types of gas ionization detectors are insensitive to oxygen, nitrogen, carbon dioxide and hydrogen sulfide. Furthermore, the beta-ray detector is not sensitive to methane.

(2) Flashing heater: The function of the flashing heater is vaporization of the liquid sample injected. Since sludge gas samples are always in the gaseous state at or above room temperature, no vaporization is required.

(3) High temperature column oven: In the analysis of low boiling point compounds, such as sludge gases, low-column-temperature-operation is generally preferred.

(4) Temperature programming: In the analysis of a multiple component gas mixture, complete separation of each component may require several optimum operating temperatures. The different temperatures of the column are created by so-called temperature programming to drive the various components out of the chromatographic column. The resolution of all sludge digestion gas mixtures could be achieved with a two-stage column and therefore temperature programming was not necessary.

On the other hand, there are several special features which may not be provided by a commercial gas chromatography unit but nevertheless are essential for the analysis of sludge gas:

(1) Large size column oven: For the separation of nitrogen from methane it was found that a partition column of 60 to 80 ft length is required. The size of column ovens of most commercial gas chromatography units, designed for the analysis of hydrocarbons and therefore requiring relatively short (4 to 12 ft) columns, are too small to accommodate these long partition columns.

(2) Non-corrosive column materials and other surfaces in direct contact with the sample gas: Stainless steel and plastic tubing, such as polyethylene or Teflon, were found to be satisfactory column materials for sludge digestion gas analysis. Copper tubing should be avoided because hydrogen sulfide may be present in the sludge gas.

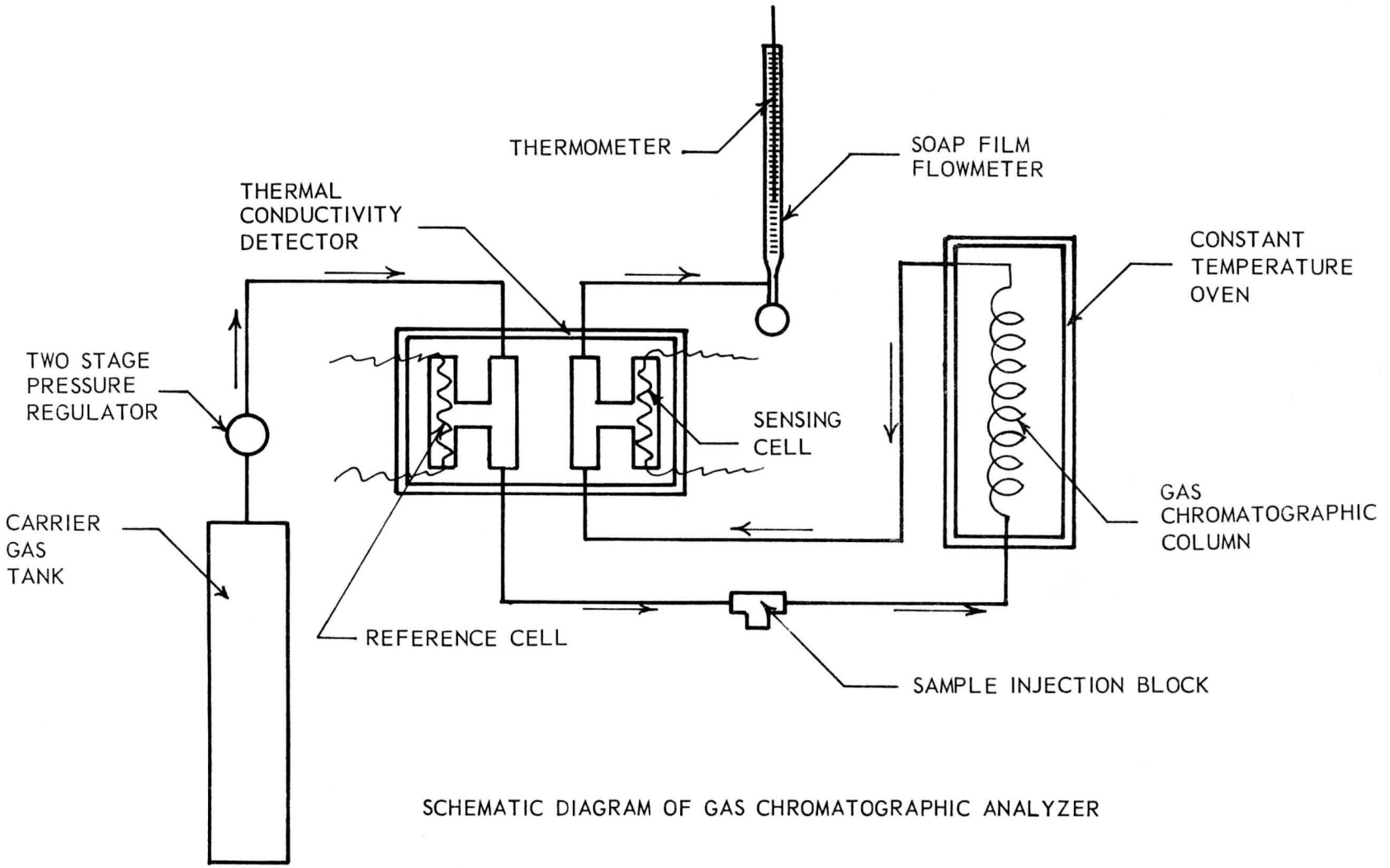
(3) High pressure gas flow system: The operation of two-stage columns demands an inlet pressure of 60 psig to assure an adequate gas flow rate. This pressure is relatively high compared to single-stage-column chromatography for which 20 to 30 psig normally suffices.

(4) Symmetric construction and equal response of the thermal conductivity detector on both the sample and reference sides: During the two-stage column operation both sides of the cell are used alternately as the sensing cell. Therefore, symmetry of construction and response are essential features of the detection cell.

(5) Range of recorder: The analysis of trace amounts of hydrogen sulfide in sludge gas demands a sensitive recorder, requiring a 0 to 1 mv range instrument. However, a 0 to 10 mv recorder is adequate for the analysis of methane and carbon dioxide.

B. Sludge Gas Analysis System

The gas chromatographic unit used for the present study consisted of three major components: (i) the chromatographic separation unit, (ii) the detector and associated electric circuitry, and (iii) the automatic recorder. The separation unit included the gas flow system, sample injector, and gas chromatographic column as shown in Figure 2. The gas flow system was composed of a two-stage pressure regulator, capable of delivering pressure greater than 60 psig, a gas delivery line confining the gas flow and, at the exit of the



SCHEMATIC DIAGRAM OF GAS CHROMATOGRAPHIC ANALYZER

Figure 2.

column, a soap film flow meter. The tubing through which the gas flow passed was copper or plastic for the section upstream from the sample injection block and stainless steel or plastic for the downstream section. The soap film flow meter was constructed by putting a rubber bulb containing soap solution on the bottom end of a 50 ml buret. The buret had a side tube connected to the exhaust end of the gas flow system. The gas flow rate could be accurately measured by recording the time required for the soap bubble to travel a finite distance on the scale of the buret.

The sample injection block was constructed by placing a rubber serum cap[5] over the center opening of a nylon tee and then covering it with a copper tubing nut. The gaseous sample was introduced by a hypodermic syringe, usually of 0.5 ml capacity, or smaller. The gas chromatographic column was placed inside a constant temperature oven. Temperatures up to 125°F could be satisfactorily maintained originally with a 100 watt light bulb[6] in an 8 in x 3 in insulated oven. The metal plate over the bulb was arranged so that the natural convection of the warm air maintained the column at a uniform temperature. A bi-metallic thermostat, placed near the light bulb to increase the control sensitivity, maintained the oven at a constant temperature within $\pm$ 1°F over a temperature range from 80° to 125°F.

An improved arrangement consisted of a fan, a two-stage 400 watt heater and a star shaped coil frame, shown in Figure 3. The temperature in the oven could be maintained at $\pm$ 0.2°F over a temperature range from 70° to 160°F. The heater was also actuated by a bi-metallic thermostat.

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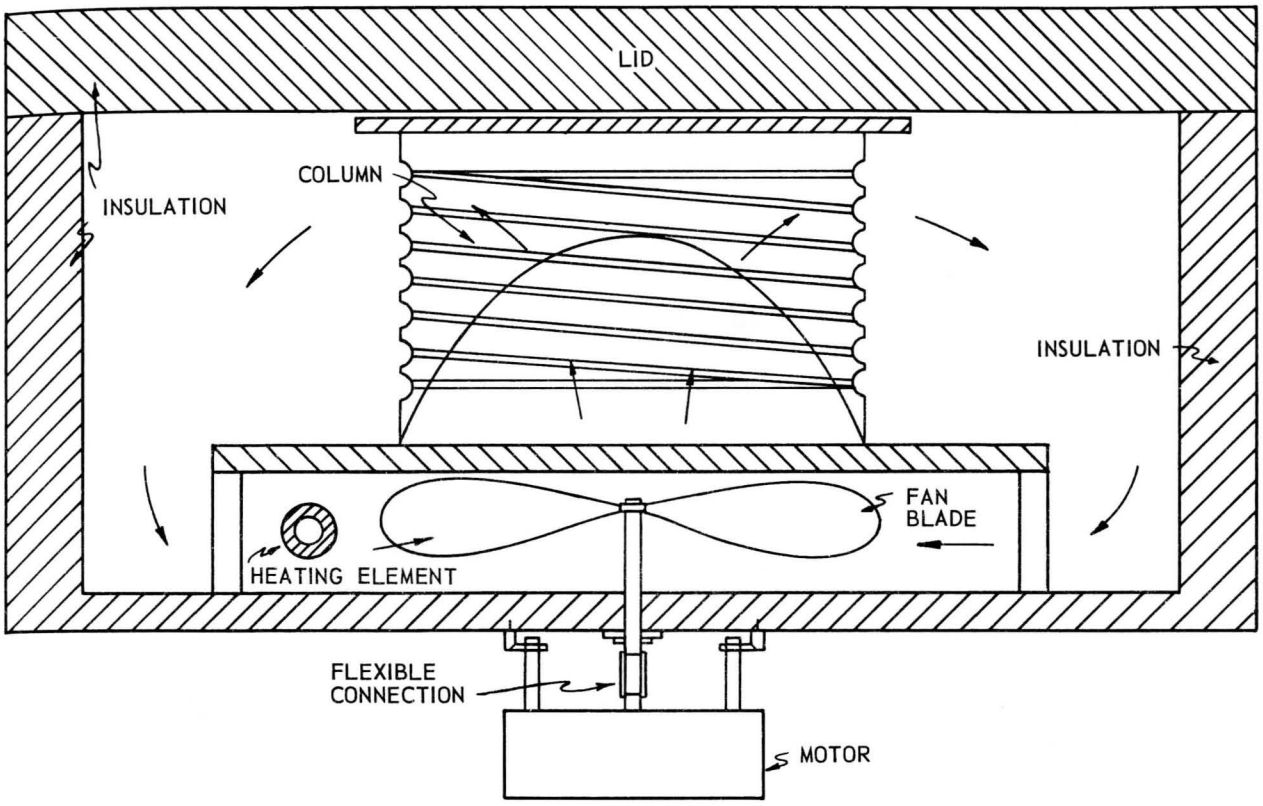
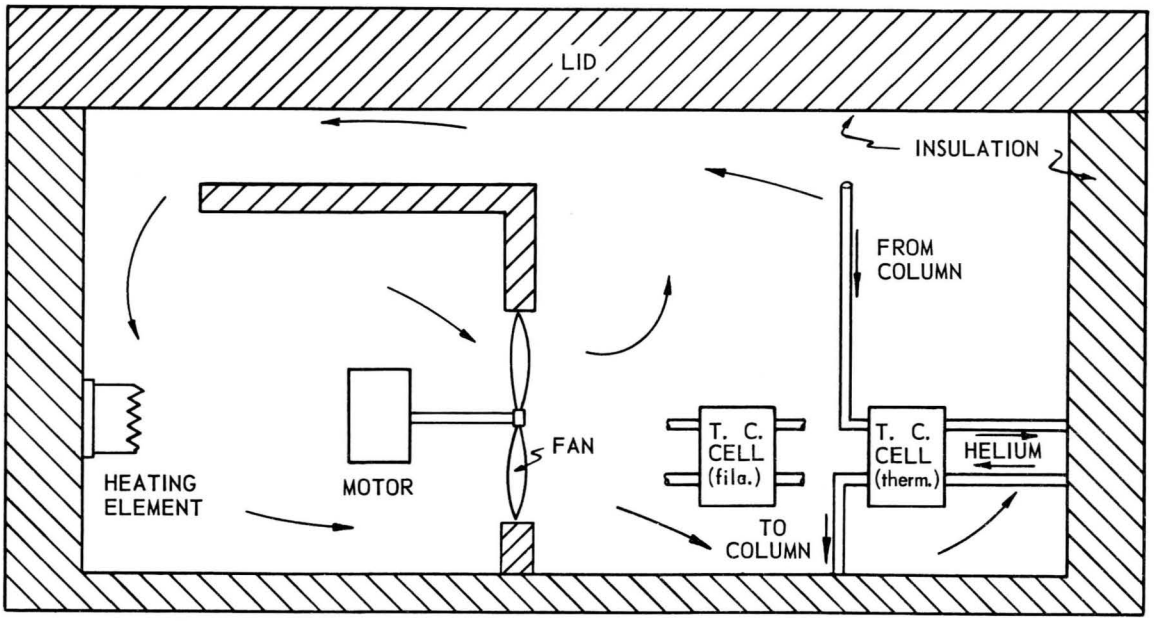
5 Silastic high temperature hypodermic injection seal, manufactured by the Loe Eng. Co., Pasadena, Calif.

6 Later converted to two banks of heaters that could be operated singly or together for fast and slow heating.



TEMPERATURE CONTROLLED COLUMN COMPARTMENT



TEMPERATURE CONTROLLED DETECTOR COMPARTMENT

Figure 3.

The entire gas flow system and column was made of polyethylene tubing. For an operating temperature above 160°F, the polytheylene must be replaced by Teflon tubing.

The detecting system consisted of two thermal conductivity cells[7] and a Wheatstone bridge which have been described previously in the literature (35) (36)(37).

To detect the components by means of their characteristic thermal conductivities, a comparison is made between the temperature of two electrically heated filaments, one surrounded by the unknown gas to be analyzed and the other by the reference gas. The temperature difference between the filament and the surrounding metal block is, as a first approximation, inversely proportional to the conductivity of gas. The filament may be either a tungsten wire or a thermistor bead. Therefore, if the two filaments of the cell are heated by equal current and exposed to gases of different thermal conductivities, the resistance bridge will measure the degree of unbalance detectable with a millivoltage meter (for circuit diagram of the resistance bridge see Figure 4-1). The deflection of the instrument will be proportional to the temperature difference and the thermal conductivity difference. Both thermistor and filament type thermal conductivity cells are able to detect all the components in sludge digestion gas. A thermistor cell is about five to ten times more sensitive than a filament type cell in the low temperature range (near room temperature) in which the analysis of sludge gas is generally carried out (see Appendix I, Table XIV). However, the thermistor cell is also much more sensitive to

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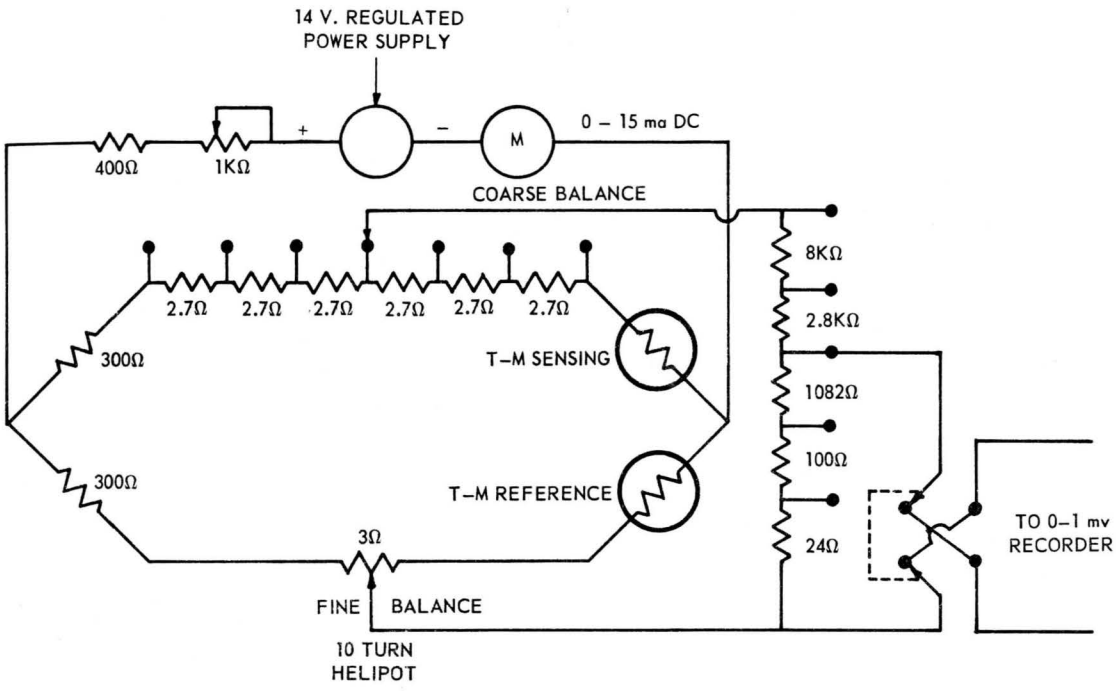
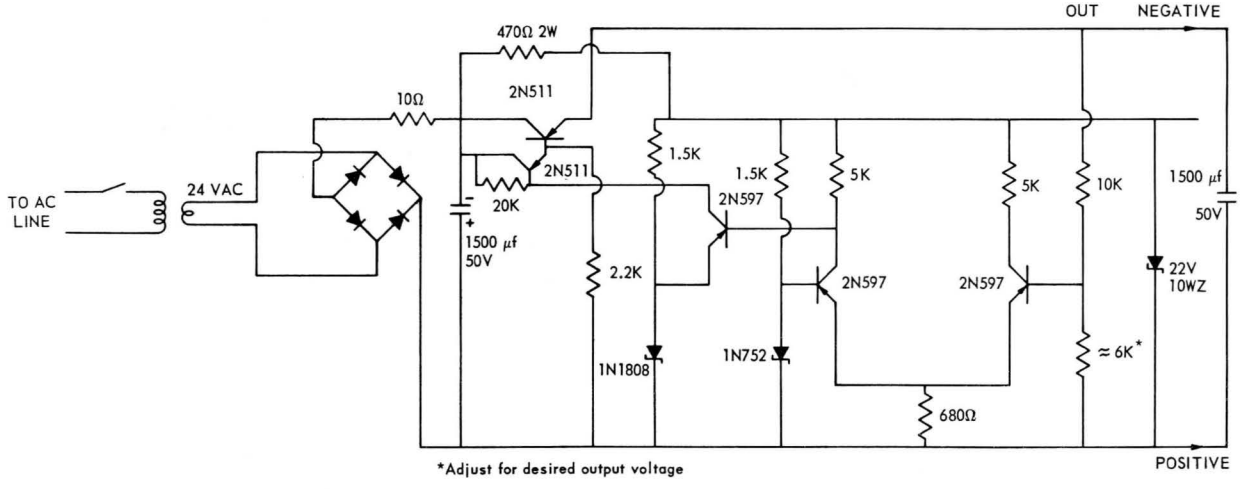
7 One of these was a filament type, Model NRL or 30S, manufactured by the Gow-Mac Instrument Co., Madison, N.J.; the other a thermistor type cell, Model TBS-4S, manufactured by Industrial Instruments Inc., Cedar Grove, N.J.



THERMAL CONDUCTIVITY CELL BRIDGE CIRCUIT



REGULATED POWER SUPPLY FOR FILAMENT TYPE THERMAL CONDUCTIVITY CELL

Figure 4.

temperature changes in the cell block. A constant cell temperature with a better than $\pm$ 0.2°F stability must be maintained to obtain a stable base line on a 0 to 1 mv recorder. On the other hand, temperature fluctuations up to $\pm$ 1°F will exert little effect on the stability of a filament type cell. The greater sensitivity of the termistor type cell offers little advantage for the routine sludge gas analysis, unless the detection of a trace amount of H_2S is desired. Most experiments for the present study were carried out by filament type cells[8] used in this laboratory.

The filament current, which must be maintained at a very constant rate to insure the stability of the base line, was supplied by a regulated constant voltage supply which transforms 110 AC voltage to 9 volt DC with a constancy better than $\pm$ 5 μv. The complete circuit diagram of the specially developed power supply is shown in Figure 4-2.

For automatic recording, a six-inch chart Varian[9] 0 to 10 mv recorder was used with a high degree of satisfaction for the routine analysis of methane and carbon dioxide in sludge digestion gas. This type of recorder can be purchased in a low price range (approximately $500) and was found to be quite adequate for routine sludge gas analysis. To detect any trace amounts of hydrogen sulfide, or other minor components, a 0 to 1 mv, 12-inch chart Wheelco[10] recorder was preferred (about $900 - $1,000). The response time of the recorder should be two seconds (full chart range) or faster.

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8 Types NRL and 30S, manufactured by Gow-Mac Instrument Co., Madison, N.J.

9 Model 11A, manufactured by Varian Associates, Palo Alto, California.

10 Model 8000-1600, manufactured by Wheelco Industrial Instruments Division, Barber-Colman Company, Rockford, Ill.

C. Automatic Digester Gas Sampling Valve

When it is necessary to analyze only a few samples daily, sampling with a hypodermic syringe is a convenient and adequate method. However, if the analysis of a large number of samples is required each day, or if samples need to be taken with a high frequency to closely follow the progress of digestion, or it is desired to automatically control the digestion process, an automatic sampling device, capable of collecting and injecting samples into the analyzer at pre-set time intervals becomes highly desirable.

The first automatic sampling valve developed was of a rotary cam type, connected with a Microbellows pump. The difficulty with this first model was the relatively large dead volume which caused contamination between two successive samples injected. The second model, previously reported in the literature (38), completely eliminated the dead volume problem. However, no machine shop was able to produce the extremely high polish surface required between the two flat plates so as to slide against each other and maintain a perfect seal against any helium leakage between the high and low pressure sides. All requirements were finally met in a third working model, shown in Figure 5, by replacing the two flat plates with two concentric cylinders, separated by rubber "O" rings set into grooves on the outer surface of the inner, solid cylinder or plunger to effectively prevent gas leakage.

This sampling valve operates on the following principle: Ports 1 and 3 are connected to two different sample streams to be analyzed, while port 2 is lined up for the passage of carrier gas into the gas chromatographic unit. When the inner cylinder slide moves toward the right, the sample previously trapped in port 1 will be transferred to port 2, and carried directly into the gas chromatographic column. On the return trip, the movement of the inner cylinder slide toward the left transports a sample collected in port 3 to

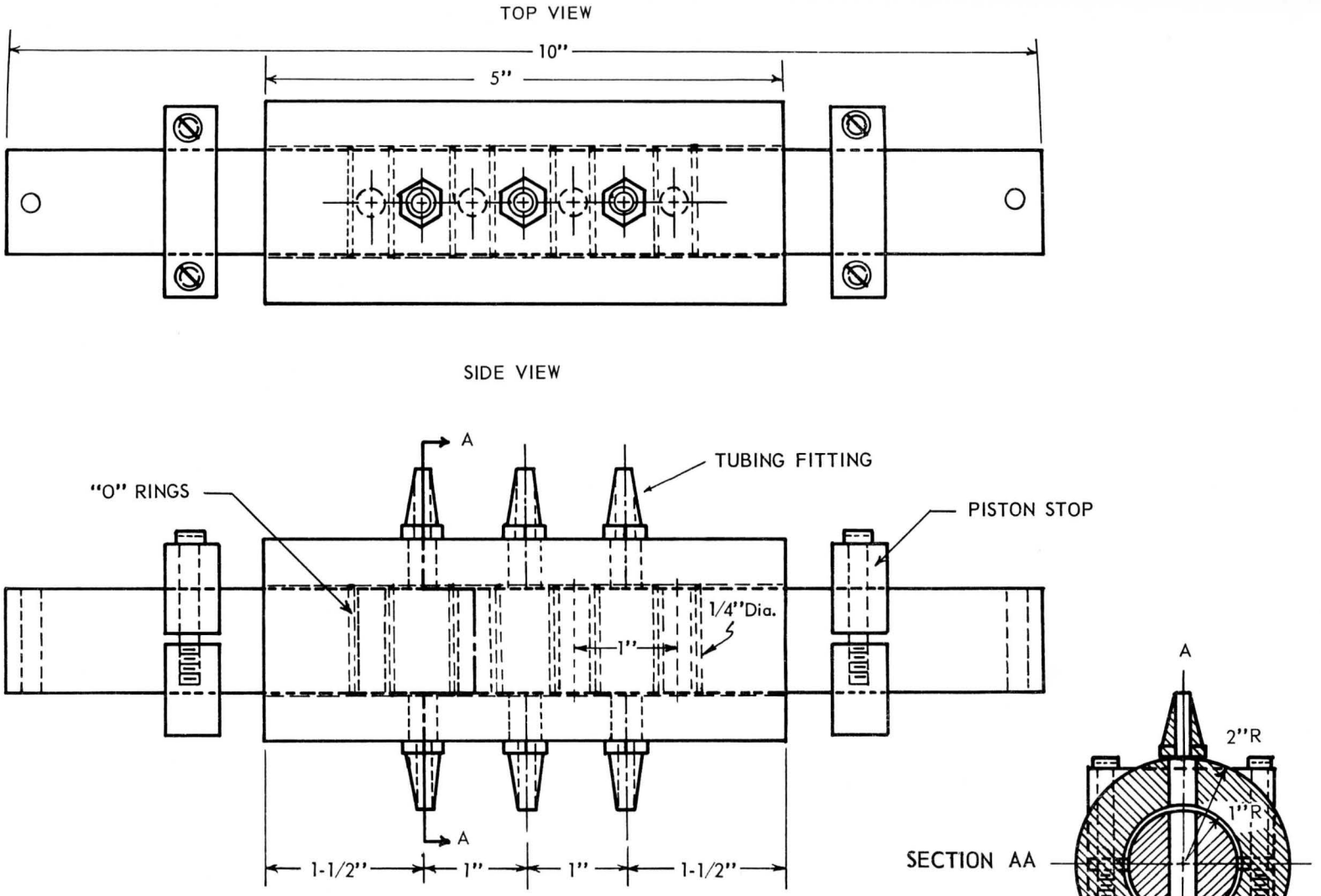

TOP VIEW
10"
5"
SIDE VIEW
A
"O" RINGS
TUBING FITTING
PISTON STOP
1/4"Dia.
1"
A
1-1/2"
1"
1"
1-1/2"
AUTOMATIC SAMPLING VALVE
A
2"R
1"R
SECTION AA
A

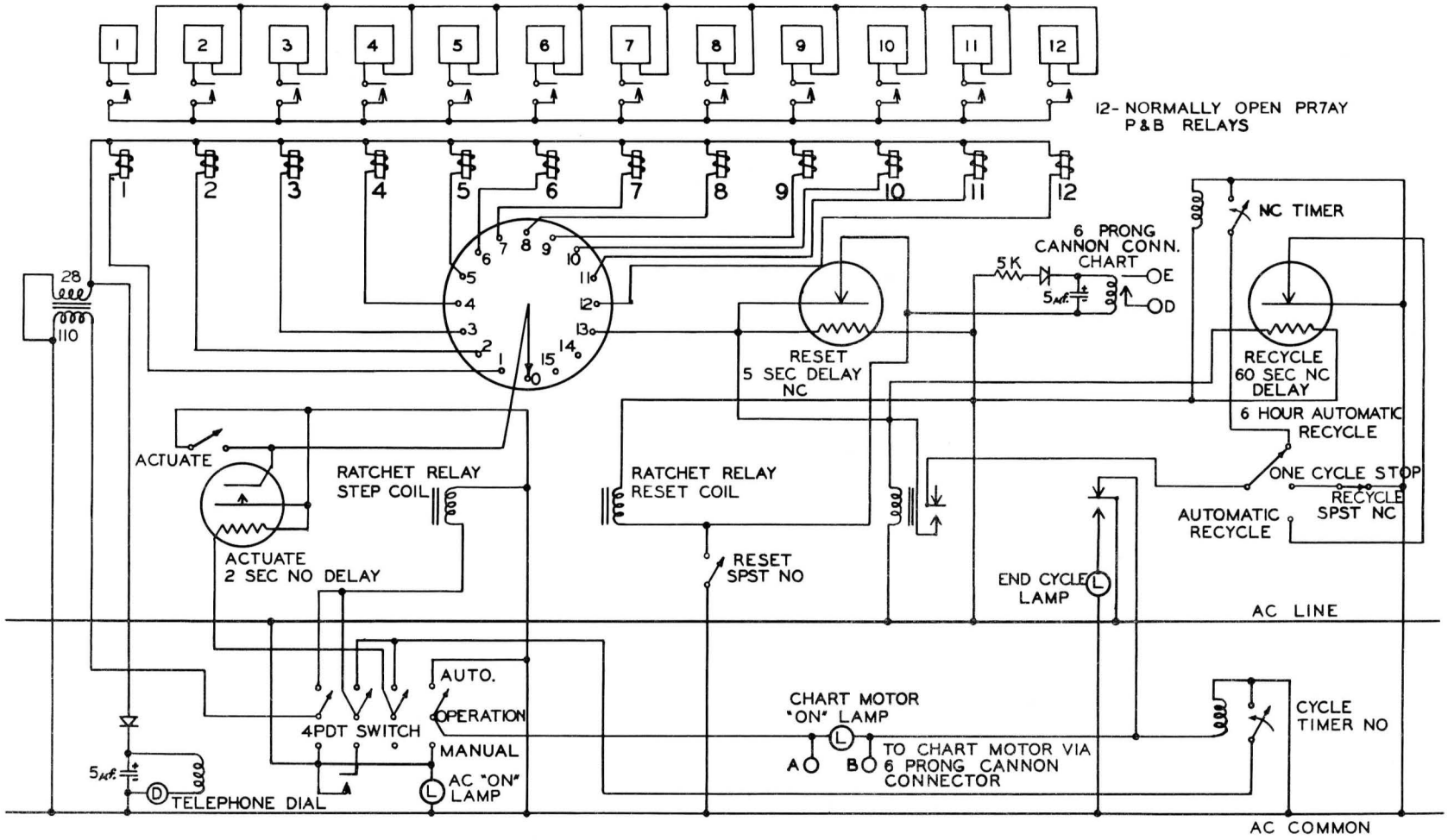
Figure 5.

port 2 for chromatographic analysis. "O" rings seated between the ports prevented the leakage of high pressure carrier gas into the sample streams. The latter was especially important when the gas production rate from laboratory digesters was measured, as leakage of helium would have provided inaccurately high gas production values.

The movement of the sampling valve was actuated by two solenoids which were controlled by a timing device. The timing device was especially designed and developed to control as many as nine automatic sampling valves and therefore could sample continuously from 18 separate digesters. The complete circuit diagram of the timing device is shown in Figure 6.

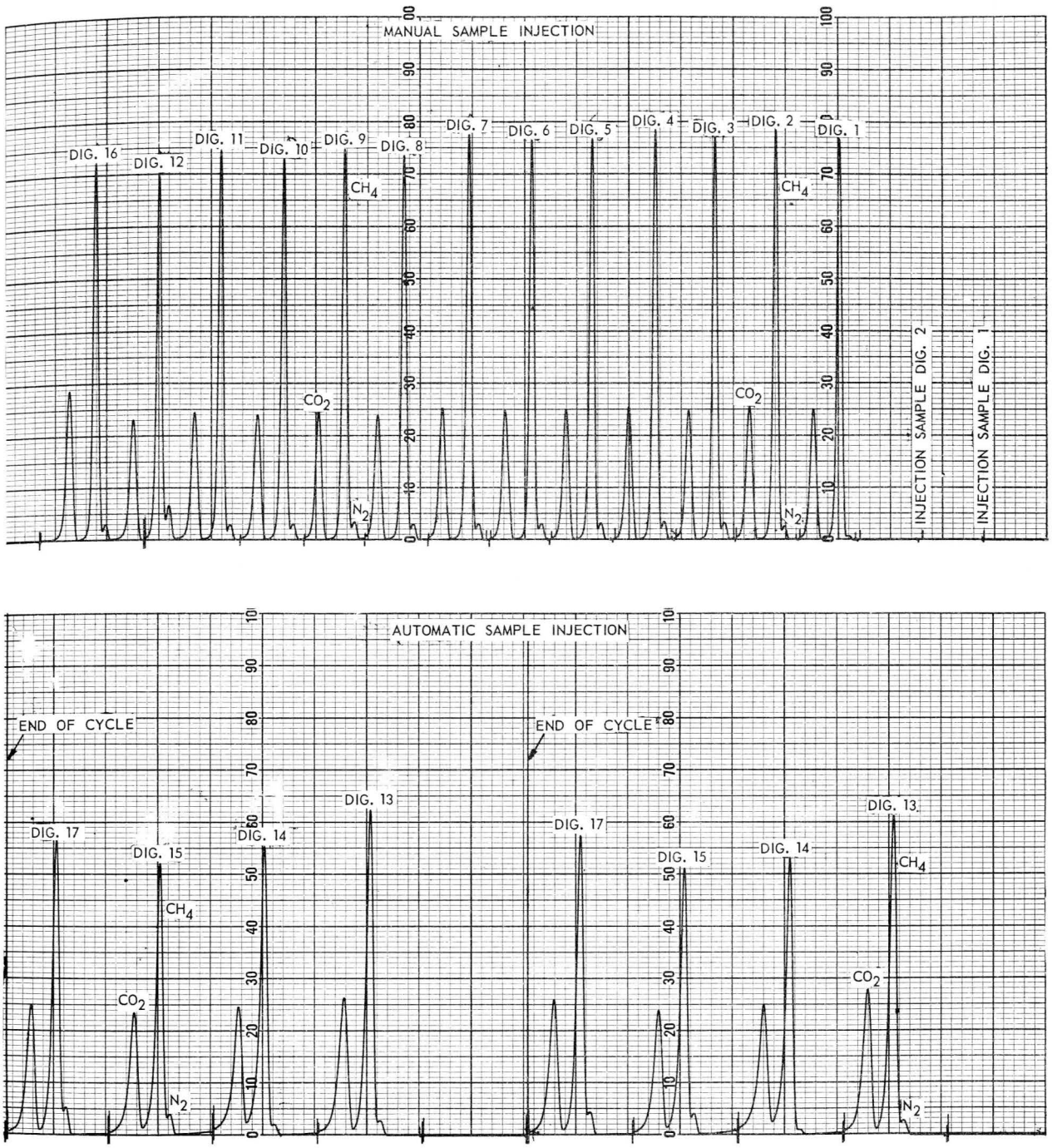
Complete gas analyses from each of 18 digesters could be repeated for any pre-set time interval, say every six hours. To save chart paper and carrier gas, the timing device also actuated and stopped the chart drive motor of the recorder and a gate valve to open and close the carrier gas flow to the analyzer. A marking device distinguished the completion of each run on the chart paper permanently. Typical chromatograms obtained with the automatic sampling system for two complete cycles from four digesters are shown in Figure 7.

The automatic sampling valve could also be manually controlled to stop the cycle at any time and to perform an analysis for a particular digester by simply dialing a number and pushing a button. With the features incorporated in this sampling valve, a highly versatile research laboratory or operational control device has been developed.



CIRCUIT DIAGRAM OF TIMING DEVICE IN AUTOMATIC SAMPLING SYSTEM

Figure 6.



GAS CHROMATOGRAPHIC ANALYSIS OF SLUDGE GASES

COLUMN: 71 FT. SILICONE GREASE ON C-22 FIREBRICK
FLOW RATE: 80 ML/MIN.
SAMPLE SIZE: 1.0 ML. EACH
COLUMN TEMPERATURE: 80°F

Figure 7.

Chapter 4

SELECTION OF GAS CHROMATOGRAPHIC COLUMNS

The heart of any gas chromatographic analysis unit is the chromatographic column. A major portion of the effort during the present studies was devoted to the determination of one or more of the most suitable column materials for sludge gas analysis. Over fifty different solid (adsorption) or liquid (partition) materials were studied and about two hundred columns were prepared and investigated. These columns can be divided into two general groups: gas-solid adsorption columns and gas-liquid partition columns.

A. Gas-solid Adsorption columns

At the beginning of these studies, various types of solid adsorption columns were prepared and evaluated. The adsorbents used for packing materials include activated charcoal, silica gel, molecular sieves (13X and 5A), silica alumina and nickel sulfate. Particle sizes of the packing varied from 14 to 100 mesh and column length from 4 inches to 12 feet. Typical chromatograms obtained with some of these columns are presented in Figure 8.

(1) Activated Charcoal: Much of the early period of study was devoted to the activated charcoal column. The first column was made in a heavy wall pyrex tube, with a 5 mm bore, packed with 42 inches of 80 mesh activated charcoal and some separation between N_2, CH_4 and CO_2 was achieved. Too great a pressure drop across the column and too long an elution time (up to 45 min for CO_2) made such a column impractical. Later, the length of the column was reduced to 25 cm. Improved separation between N_2, CH_4 and CO_2 were obtained, although considerable tailing for the CO_2 still prevailed. The first column selected for routine analysis was a 7-in column, packed with particles of

Column Data for Figure 8

Figure 8-1: Molecular sieves 5A
Column: Molecular sieves 5A, 14-28 mesh, 6 feet, 4mm I.D.; Carrier gas: Helium;
Column temperature: 76°F; Filament current: 120 ma.
A. Sample: 5.0 ml synthetic mixture (70.0% H_2, 6.7% O_2, 0.1% A, 23.4% N_2)
Flow rate: 76 ml/min
B. Sample: 1.0 ml synthetic mixture (66.4% H_2, 7.1% O_2, 0.3% A, 26.2% N_2)
Flow rate: 100 ml/min
C. Sample: 1.0 ml synthetic mixture (1.1% O_2, 0.06% A, 4.1% N_2, 94.7% CH_4)
Flow rate: 100 ml/min

Figure 8-2: Molecular sieves 13X
Column: Molecular sieves 13X, 14-28 mesh, 6 feet, 4 mm I.D.; Carrier gas: Helium;
Column temperature: 76°F; Flow rate: 72 ml/min; Filament current: 120 ma.
A. Sample: 5.0 ml synthetic mixture (91.0% H_2, 1.9% O_2, 0.1% A, 7.0% N_2)
B. Sample: 1.0 ml sludge gas (0.06% O_2+A, 0.45% N_2, 67.20% CH_4, 32.29% CO_2*)
* CO_2 is irreversibly adsorbed by the column; therefore, no chromatogram of CO_2 appears.

Figure 8-3: Silica gel
Column: Silica gel, 28-48 mesh, 4 mm I.D.; Carrier gas: Helium;
Filament current: 120 ma.
A. Column length: 12 feet
Sample: 1.5 ml sludge gas (1.93% N_2, 62.60% CH_4, 35.43% CO_2)
Flow rate: 80 ml/min; Column temperature: 130°F
B. Column length: 8 feet
Sample: 0.5 ml air plus 0.5 ml CH_4
Flow rate: 65 ml/min; Column temperature: 80°F

Figure 8-4: Activated charcoal
Column: Activated charcoal, 28-48 mesh, 7 inches, 4 mm I.D.
Sample: 0.5 ml sludge gas (7.7% N_2, 57.7% CH_4, 34.6% CO_2); Flow rate: 85 ml/min
Carrier gas: Helium; Column temperature: 75°F; Filament current: 120 ma.

Figure 8-5: Changes in polarity of H_2 peaks caused by the change in sample size
Column: Molecular sieves 13X, 14-28 mesh, 6 feet, 4 mm I.D.
Samples: H_2 and air mixture (95.0% H_2, 1.1% O_2+A, 3.9% N_2) with sample size varied from 0.1 ml to 4.0 ml; Flow rate: 72 ml/min
Carrier gas: Helium; Column temperature: 75°F; Filament current: 170 ma

Figure 8-6: Silica alumina
Column: Silica alumina, 40 mesh, 2 feet
Flow rate: 90 ml/min; Carrier gas: Helium; Column temperature: 75°F;
Filament current: 120 ma
A. Sample: 0.5 ml NH_3 plus 0.5 ml N_2
B. Sample: 0.5 ml N_2
C. Sample: 0.5 ml NH_3

Figure 8-7*: Detection of small amount of H_2 from air, N_2 or sludge gas
Column: Molecular sieves 13X, 14-28 mesh, 6 feet, 4 mm I.D.; Flow rate: 84 ml/min
Carrier gas: Nitrogen; Column temperature: 74°F; Filament current: 130 ma
A. Sample: 5 ml air plus 26 ppm of H_2
B. Sample: 5 ml nitrogen(**) plus 0.05 ml O_2 and 26 ppm of H_2
C. Sample: 5 ml sludge gas (65.7% CH_4, 25.8% CO_2, 8.0% N_2, 0.5% O_2+A plus 26 ppm H_2)

* Polarity of the recorder signal was reversed; therefore, the positive peaks appearing in this figure are really negative and vice versa.
**Nitrogen is used as the carrier gas; therefore no nitrogen peak appears.

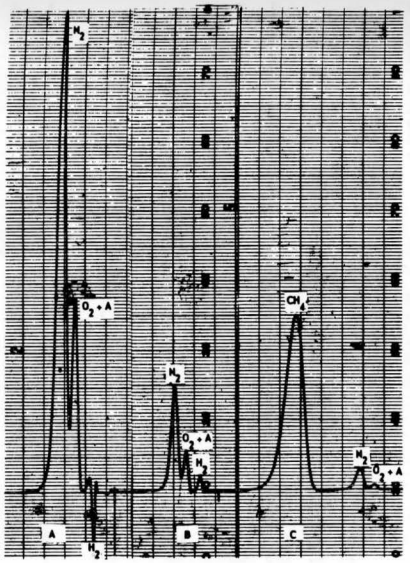


FIG. 8-1. MOLECULAR SIEVE 5A

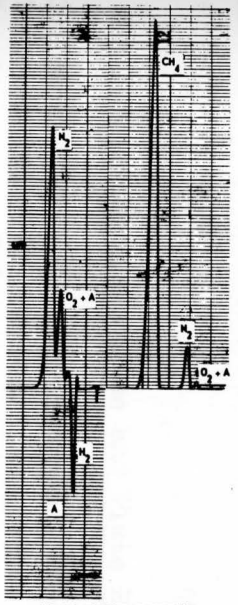


FIG. 8-2. MOLECULAR SIEVES 13X

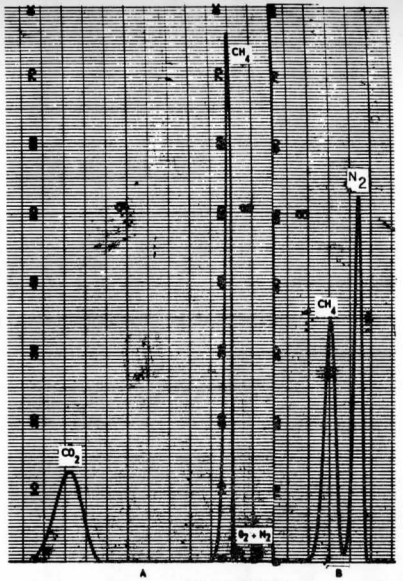


FIG. 8-3. SILICA GEL

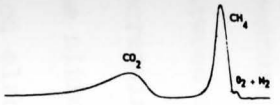


FIG. 8-4. ACTIVATED CHARCOAL

FIG. 8-5. MOLECULAR SIEVE 13X
(Change of Polarity of H_2 Peaks)

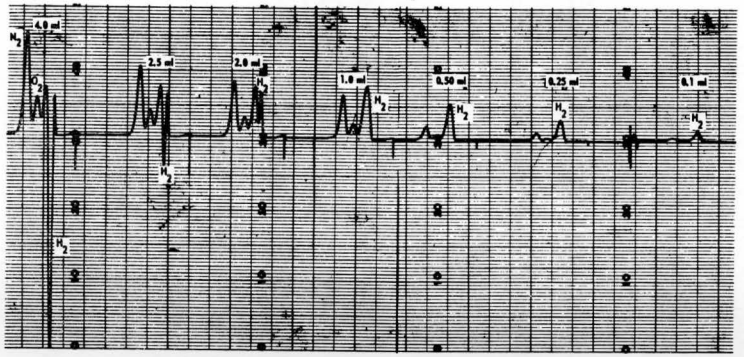


FIG. 8-6. SILICA ALUMINA

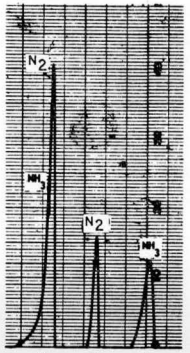
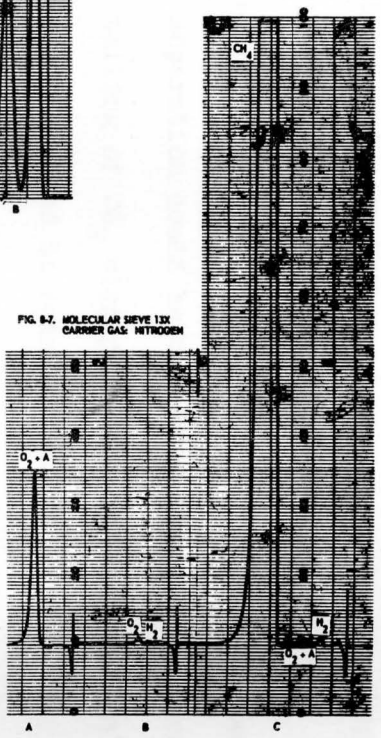


FIG. 8-7. MOLECULAR SIEVE 13X
CARRIER GAS: NITROGEN



ADSORPTION CHROMATOGRAPHY.

Figure 8.

28-48 mesh size in 4 mm I.D. copper tubing. With a flow rate of 80 ml/min, a pressure drop of less than 1 psi across the column was achieved. Separation between nitrogen and methane was incomplete as shown in Figure 8-4. By either increasing the column length or reducing the mesh size of the charcoal particles, the nitrogen to methane separation could be completed, but this column modification also increased the tailing of CO_2 significantly. Therefore, optimum length of this column was established at between 5 and 7 inches. Activated charcoal adsorbs H_2S and NH_3 irreversibly; thus no peaks for these two components will show up in the chromatogram, even if these gases exist in the sludge gas sample.

The retention volume and plate efficiency for CH_4 and CO_2 in a 7-in charcoal column under normal operating conditions for sludge gas analysis are listed in Table I.

TABLE I

Retention Volume and Plate Efficiency for 7-in Charcoal Column

Column: 7-in activated charcoal, 28-48 mesh, 4 mm I.D. copper tubing
Temperature: 75°F
Carrier gas: Helium
Flow rate: 85 ml/min

Component	Retention[11] Volume (ml)	Apparent[11] Retention Volume (ml)	Number of[11] Theoretical Plates	Plates per foot[11] of Column Length
N_2[12]	17.0	0	18.0	31.9
CH_4	31.1	14.1	31.4	38.4
CO_2	139.0	122.0	29.6	50.7

[11] See Glossary

[12] See page 21 footnote 4 for explanation.

(2) Silica gel: Silica gel is a moderate adsorbent compared to activated charcoal. Therefore, a longer column is generally required. At room temperature, or slightly above ($80^{\circ}F$), a 4-ft silica gel column, 28-48 mesh particle size is adequate to separate CO_2 from CH_4 and N_2, but the chromatograms of CH_4 and N_2 overlap. Complete separation between CH_4 and N_2 was achieved by increasing the column length to 12 feet. At the same time, however, the retention time for CO_2 increased to 17.5 min at a flow rate of 75 ml/min. By raising the column temperature to $130^{\circ}F$, the retention time for CO_2 was reduced to 6.8 min with the 12-ft column, and a much sharper CO_2 peak was obtained. However, the degree of separation between N_2 and CH_4 was slightly decreased.

At room temperature, silica gel is inclined to absorb moisture from wet gas samples collected directly over the sludge in the digester. These samples are nearly saturated with water vapor. Consequently, with the continued use of the column the resolving power will decrease, indicated by shorter and shorter retention times for CO_2 and poorer separation between N_2 and methane. The life of the silica gel column will be considerably prolonged when the column is operated under higher temperature. At $130^{\circ}F$, no significant change in the retention time of CO_2 was observed for 3 to 4 weeks of continuous operation with 18 analyses (20 to 30 sample injections) performed daily. Laboratory data to substantiate no measurable changes for 27 days are shown in Table II.

TABLE II

Changes of CO_2 Retention Time with Age in a 12-ft Silica Gel Column

(Column Temperature = 130°F)

Date	CO_2 Retention Time
4/2/58	412 seconds
4/3/58	419 seconds
4/5/58	411 seconds
4/7/58	414 seconds
4/9/58	406 seconds
4/11/58	410 seconds
4/12/58	416 seconds
4/16/58	416 seconds
4/17/58	413 seconds
4/18/58	413 seconds
4/21/58	414 seconds
4/23/58	412 seconds
4/28/58	408 seconds
4/30/58	392 seconds

To rejuvenate a silica gel column, the moisture may be removed by raising the column temperature to 220°F for three to four hours and simultaneously purging the column with carrier gas. Since the chromatograms of sludge gas components obtained from the silica gel column are more symmetrical than that from an activated charcoal column (compare Figures 8-3 with 8-4), the 12-ft silica gel column, packed with 28-48 mesh particles, replaced the charcoal column for routine analysis. The silica gel column was operated at 130°F with a flow rate of 80 ml/min, using helium as carrier gas. Beginning with October, 1957, this column served the gas analysis for three experimental sludge digestion runs covering a half year period with 16 to 20 analyses performed daily. By means of the periodic rejuvenation method mentioned above, the column was still in excellent operating condition without any permanent deterioration noted. The silica gel column separates the major components of sludge gas, i.e., nitrogen (including

oxygen, if any), methane and carbon dioxide. It adsorbs irreversibly H_2S and NH_3.

Several columns containing combinations of silica gel and activated charcoal were investigated. However, no advantage could be obtained from such a combination because of the very strong adsorptivity of activated charcoal toward carbon dioxide.

Table III lists the retention volume and plate efficiency of a 12-ft silica gel column.

TABLE III

Retention Volume and Plate Efficiency for 12-ft Silica Gel Column

Column: 12-ft silica gel, 28-48 mesh, 4 mm I.D. copper tubing
Temperature: 130°F
Carrier gas: Helium
Flow rate: 80 ml/min

Component	Retention Volume (ml)	Apparent Retention Volume (ml)	Number of Theoretical Plates	Plates per Foot of Column Length
N_2	120	0	104	8.7
CH_4	132	12	152	12.7
CO_2	152	32	165	13.7

(3) Molecular Sieves: Molecular sieves are a form of silicate crystal which provide regular networks of channels with diameters in the same order of size as that of molecules. Consequently, such crystals supposedly can act as "sieves" and bring about a separation of molecular species by occluding small molecules, while not adsorbing larger molecules or molecules with shapes that do not "fit" (39). Apparently, this general

assumption is not always true. For example, type 5A molecular sieves which have a channel diameter of 5Å, adsorb NH_3 (molecular diameter = 3.80Å) and CO_2 (m.d. = 3.28Å) rapidly, but only slightly adsorb oxygen (m.d. = 2.92Å), nitrogen (m.d. = 3.15Å) and helium (m.d. = 2.65Å) at room temperature.

The two types of molecular sieves which have been used are types 5A and 13X [13]. The sieves, in the form of 1/16-in pellets originally, were ground and screened to 12-28 mesh, then dried at 600°F for 2 to 3 hours. Initially 7-in long columns were studied. At room temperature, with a helium flow rate of 80 ml/min, type 5A sieves separated O_2, N_2 and CH_4 (incompletely between N_2 and CH_4), while type 13X could not separate any of these components under the same conditions. Both columns adsorbed CO_2, H_2S and NH_3 irreversibly. After their length was extended to 6 ft both columns showed good separation for H_2, O_2, N_2 and CH_4, but still adsorbed CO_2, H_2S and NH_3, irreversibly. Some of these results are shown in Figures 8-1 and 8-2. Argon was eluted at the same time as oxygen and therefore could not be identified separately[14]. From a comparison of the retention volumes of both 5A and 13X sieve columns, as shown in Table IV, it is evident that type 5A exhibits the greater resolving power.

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[13] Products of Linde Air Products Co., Tonawanda, New York.

[14] By using nitrogen instead of helium as the carrier gas, it is possible to distinguish argon from oxygen because the former produces a negative peak whereas the latter would produce a positive peak. A sample taken from an experimental digester was analyzed in this way by a 12-ft molecular sieve 5A column and a negative peak appeared. The argon gas present in the sample must have originated from atmospheric air. The presence of argon gas thus confirmed the statement on page 21, footnote 4, that the nitrogen present in the sludge sample is coming from the atmosphere rather than from the decomposition of sludge.

TABLE IV

Retention Volume and Plate Efficiency for 6-ft Molecular Sieve Columns

Column: 6 ft Molecular Sieves, 12-28 mesh, 4 mm I.D. copper tubing
Temperature: 76°F
Carrier gas: Helium
Flow rate: 72 ml/min

Component	Retention Volume (ml)		Apparent Retention Volume (ml)		Number of Plates		Plates per foot of Column Length	
	13X	5A	13X	5A	13X	5A	13X	5A
H_2	59.5	53.0	0	0	92	106	15.3	17.7
O_2	87.6	104.5	28.1	51.5	121	142	20.2	23.6
N_2	110.0	139.0	60.5	86.0	110	180	18.3	30.0
CH_4	191.0	303.0	131.5	250.0	191	158	31.8	26.4

Since molecular sieves are the only adsorbent so far known which can separate nitrogen and oxygen, they could be very useful columns to check on the presence of oxygen in a digester.

Another feature of interest of molecular sieve columns are their resolving power for hydrogen. By using nitrogen, instead of helium as the carrier gas, the molecular sieve columns are very sensitive to the detection of H_2 gas. Further details will be discussed in Chapter 6, Part A, "The Analysis of Hydrogen."

(4) Silica Alumina: A 2-ft column, packed with 40 mesh size particles, was studied. At room temperature and with a 90 ml/min helium flow rate, the silica alumina column was not able to separate any of the following components: N_2, CH_4, CO_2, NH_3, or H_2S. As the flow rate was decreased to 10 ml/min, some separation between N_2 and NH_3 was noticeable. This column material may be suitable for the analysis of NH_3 from sludge gas if the proper column temperature and length are employed.

(5) Nickel Sulfate: A 50-in column, packed with 4-ft $NiSO_4$ and 2-in silica gel, separated H_2S from N_2, CH_4 and CO_2. However, the separation between N_2, CH_4 and CO_2 was poor, their retention volumes being approximately equal. This column may be useful for the separation of H_2S from sludge gas.

(6) Duolite Cation Resin: The resolving power of sludge gas by a 24-in duolite cation exchange resin[15] column at a helium flow rate of 60 ml/min was studied. None of the components in sludge gas were eluted in a reasonable time. Therefore, it was concluded that the adsorbent quality of this exchange resin is too great for use as a chromatographic column material for digester gases.

(7) Wash Oil: Both naphthalene and paraffin base wash oils were coated on activated charcoal (coating ratio of 10:100 of liquid to solid by weight) in an effort to decrease tailing. The adsorption power of the column was completely lost; all components of sludge gas eluted simultaneously.

B. Gas-Liquid Partition Columns

In the application of gas chromatography to sludge digestion gas analysis partition columns generally have an advantage over adsorption columns because the former produce chromatograms which are sharper and more symmetrical.

Since it has been generally believed that partition columns are better suited for the analysis of the high-boiling point organic vapors, the literature is devoid on their application to low boiling point gases,

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[15] Duolite O-60 phosphoric cation exchanger, a product of the Chemical Process Company, 901 Spring Street, Redwood City, California.

such as nitrogen or methane. However, during the course of the studies described herein, a number of different liquid coatings were evaluated which included: (a) di-n-butyl maleate, (b) tri-m-cresyl phosphate (T.C.P.), (c) glycerine, (d) stearic acid, (e) tri-iso-butylene, (f) tetra-iso-butylene, (g) dimethyl sulfolane, (h) squalane, (i) silicone grease, (j) silicone oil and (k) Triton X-100. The formulas and boiling points of these partition liquids are listed in Table V.

In view of the fact that there was little information, and even less actual data available on the behavior of partition liquids toward individual, low-boiling point gases, or mixtures of these gases at the initiation of these studies, it was necessary to undertake a systematic examination of the ability of various stationary phase liquids to resolve sludge gas mixtures.

(1) General Methods for the Preparation of Partition Columns: The liquid coating was dissolved in pure ether or carbon tetrachloride, the former solvent being preferred. The total volume of coating liquid plus solvent was made to equal the volume of the solid support material, in order to completely cover the solids during coating. After the ratio of coating liquid to solid support was fixed, the amount of solvent needed was obtained by difference. The solution was then coated on either Celite[16] or C-22 firebrick[17] which had been ground to various mesh size ranges. The ranges generally used for C-22 firebrick included: 18-35, 28-48, 35-50. The coated particles, after having been thoroughly dried

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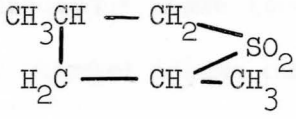
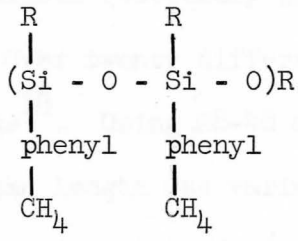
[16] Celite 545, a diatomite filter aid, is a product of the Celite Division, Johns-Manville Company, 22 East 40th Street, New York 16, N.Y.

[17] C-22 insulating firebrick is a product of Johns-Manville Company, 22 East 40th Street, New York, N.Y.

TABLE V

Formula and Boiling Points of Partition Liquids

Chemical or Trade Name	Formula	Boiling Point °C
tri-m-cresyl phosphate	$(CH_3C_6H_4)_3PO_4$	275/17 mm Hg[a]
glycerine	$(CH_2OH)_2CHOH$	290/760 mm Hg[b]
stearic acid	$CH_3(CH_2)_{16}COOH$	383/760 mm Hg[b]
tri-iso-butylene	$(C_4H_8)_3$	178/760 mm Hg[a]
tetra-iso-butylene	$(C_4H_8)_4$	-
dimethyl sulfolane		-
squalane	$C_{30}H_{62}$	210/1 mm Hg[c]
Dow Corning silicone oil 550		-
Dow Corning silicone grease	-	-
Triton X-100	$C(CH_3)_3\ C(CH_3)_3 \longleftrightarrow O\ CH_2CH_2(9R\text{-}10R)OH$	-

(a) Hodgman, C.D., Handbook of Chemistry and Physics, 42 ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1961

(b) Eastman Organic Chemicals, 42 ed., Distillation Products Industries, Rochester, New York, 1960

(c) Keulemans, A.I.M., Gas Chromatography, 2nd ed., Reinhold Publishing Co., New York, New York, 1959, p. 222

in the open air, were packed into 4 mm I.D. copper tubing. According to Keulemans (40), the ratio of stationary liquid to inert support may vary from 20:100 to 50:100 parts by weight. When the liquid ratio becomes too low, say 15:100, the support material may exhibit sufficient adsorptivity to cause tailing of the solution peaks. For small samples, up to about 0.5 ml, a liquid support material weight ratio as low as 15:100 can be used to advantage. To separate large sample volumes it is advisable to use a fairly high liquid to solid support ratio. In general, a ratio of 40:100 by weight was used throughout these investigations. With the necessary precautions, a properly charged column can be used for several thousand gas analyses. A discussion of the results obtained from the systematic examination of various stationary phase liquids follows:

(2) Silicone Grease: Over twenty different columns were prepared with silicone grease coatings[18]. Using 28-48 mesh C-22 firebrick as the stationary support, the column length was varied. Also, various ratios of liquid coating to inert solid were studied. A 10-ft column with a 10:100 by weight ratio between liquid and solid was not able to resolve any of the components normally contained in sludge gas. As the liquid to solid ratio was increased to 35:100 the nitrogen and carbon dioxide began to be separated. The retention volume between N_2 and CO_2 peaks was found to be equal to 20 ml for a 7.5 ft column at 70°F. The separation was further improved when a heavier coating of a 60:100 ratio was used. Ultimately, the complete separation between N_2, CO_2 and H_2S was achieved by 24-ft column of this type, although the separation between N_2 and CH_4 was incomplete.

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[18] Dow Corning silicone stopcock grease, a product of Dow Corning Corp., Midland, Michigan.

In an effort to improve the separation between N_2 and CH_4, short lengths varying from 1/8-in to 4-in activated charcoal, 28-48 mesh, were added in series to the silicone grease column. The activated charcoal greatly improved the separation between N_2 and CH_4 but seriously reduced the peak height and impaired the symmetry of the CO_2 and H_2S chromatograms. It was further established that if the activated charcoal was added to the exit side, instead of at the entrance to the column, it would improve resolution and produce less tailing of the CO_2. Typical chromatograms obtained with these columns are shown in Figure 9.

The desired separation between N_2 and CH_4 was finally achieved by increasing the length of column to 71 feet without any charcoal. At this length, the N_2 and CH_4 still overlapped slightly. However, the column provided the required degree of accuracy for the quantitative analysis, based on the measurement of peak heights, as may be seen in Figure 7. A further increase of column length to 81 feet did not improve the separation between any of the components because the column efficiency decreased due to an increase in the pressure drop across the column.

It was determined that silicone grease columns absorb NH_3 irreversibly, therefore no peak emerged from the column unless a 5 ml or larger sample of NH_3 was used. Some degree of irreversible adsorption of H_2S was also noted. One or two milliliters of H_2S should be injected into the column to presaturate it before each analysis. Table VI summarizes the more important observations from silicone grease columns, with or without the addition of a short section of activated charcoal adsorbent.

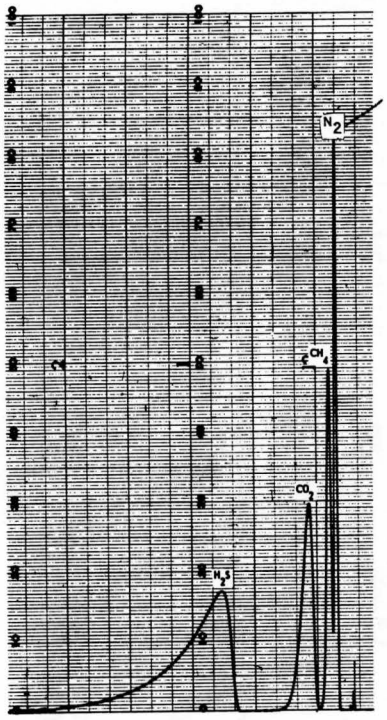

FIG. 9-1.

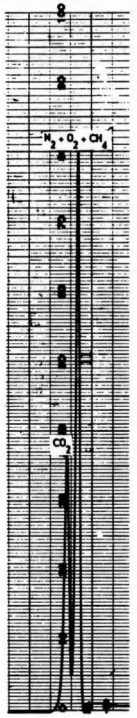

FIG. 9-3.

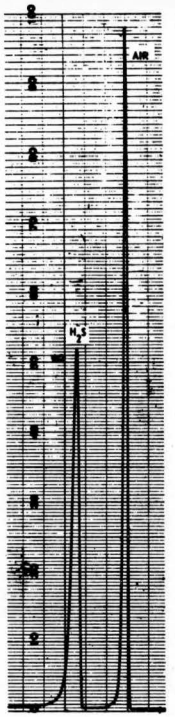

FIG. 9-4.

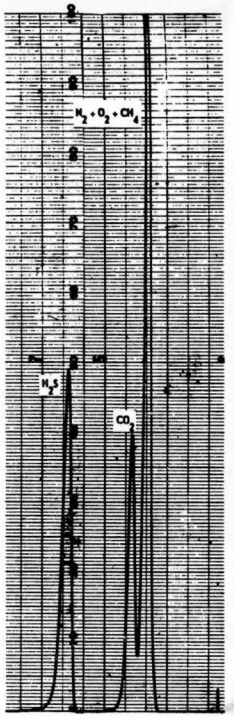

FIG. 9-6.

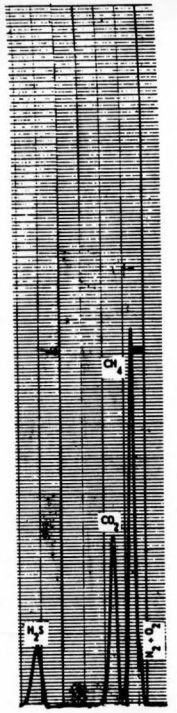

FIG. 9-7.

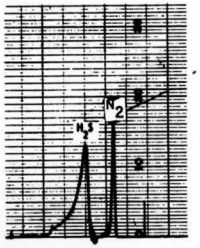

FIG. 9-2.

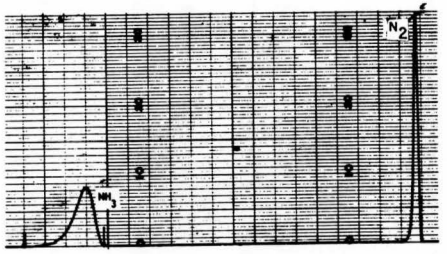

FIG. 9-5.

VARIOUS SILICONE GREASE COLUMNS.

Figure 9.

Column Data for Figure 9

Figure 9-1:
Column: Silicone grease coating on C_{22} firebrick (ratio 60:100), 4-3/4 ft. plus 3 in. activated charcoal; both 28-48 mesh, 4 mm I.D.
Sample: Mixture of 1.0 N_2, 1.0 ml CH_4, 1.0 ml CO_2 and 3 ml H_2S
Flow rate: 80 ml/min; Column temperature: 75°F; Carrier gas: Helium
Filament current: 100 ma

Figure 9-2:
Column: Silicone grease coating on C_{22} firebrick (ratio 60:100), 24 ft. plus 1/2 in. activated charcoal, 28-48 mesh, 4 mm I.D.
Sample: Mixture of 0.5 ml N_2 with 1.0 ml H_2S
Flow rate: 206 ml/min; Column temperature: 108°F; Carrier gas: Helium
Filament current: 120 ma

Figure 9-3:
Column: Silicone grease coating on C_{22} firebrick (ratio 60:100), 28-48 mesh, 12 ft., 4 mm I.D.
Sample: 1.0 ml sludge gas (3.1% N_2, 69.2% CH_4, 27.7% CO_2)
Flow rate: 85 ml/min; Column temperature: 38°F; Carrier gas: Helium
Filament current: 120 ma

Figure 9-4:
(Column, flow rate, carrier gas, temperature and current same as for Fig. 9-3)
Sample: Mixture of 1.0 ml N_2 and 0.5 ml H_2S

Figure 9-5:
Column: Silicone grease coating on C_{22} firebrick (ratio 60:100), 28-48 mesh, 24 ft. 4 mm I.D.
Sample: Mixture of 0.4 ml N_2 and 1.5 ml NH_3
Flow rate: 100 ml/min; Column temperature: 75°F; Carrier gas: Helium
Filament current: 120 ma

Figure 9-6:
(Column, carrier gas, temperature and current same as for Fig. 9-5)
Sample: 1.5 ml sludge gas (2.1% N_2, 70.5% CH_4, 27.4% CO_2)
Flow rate: 70 ml/min

Figure 9-7:
Column: Silicone grease coating on C_{22} firebrick (ratio 60:100), 28-48 mesh, 24 ft., plus another silicone grease column (ratio of silicone to C_{22} - 1:1), 14-28 mesh, 11 ft., 4 mm I.D.
Sample: 1.5 ml sludge gas (2.9% N_2, 67.1% CH_4, 30.0% CO_2) plus 0.5 ml H_2S
Flow rate: 90 ml/min; Column temperature: 78°F; Carrier gas: Helium
Filament current: 120 ma

TABLE VI

Retention Volumes of Silicone Grease Columns with and without Activated Charcoal Section

Retention Volume (ml)

Type of Column	24 ft[(a)]	35 ft	71 ft	4-3/4 ft + 3 in AC[(b)]	12 ft + 3 in AC	24 ft + 1/2 in AC
Component						
N_2	138	200	85[(c)]	43	89	196
CH_4	150	214	207[(c)]	57	114	-
CO_2	184	275	274[(c)]	108	221	254
H_2S	300	477	-	380	-	368

Apparent Retention Volume (ml)

Type of Column	24 ft[(a)]	35 ft	71 ft	4-3/4 ft + 3 in AC[(b)]	12 ft + 3 in AC	24 ft + 1/2 in AC
Component						
N_2	0	0	0	0	0	0
CH_4	12	14	22[(c)]	14	26	-
CO_2	46	75	89[(c)]	55	143	54
H_2S	162	277	-	337	-	172

(a) 24 ft silicone grease column, 28-48 mesh of C-22 firebrick, 35:100 liquid to solid ratio.

(b) 4-3/4 ft silicone grease column, 28-48 mesh of C-22 firebrick, 35:100 liquid to solid ratio but to which has been added a 3 in activated charcoal, 28-48 mesh at the column exit. (The activated charcoal additions reported in this Table were all at the column exit.)

(c) The volume reported here has been corrected for the effect of the pressure gradient across the column. The correction is necessary because of the excess length of the particular column.

(3) Tri-meta-cresyl phosphate (T.C.P.): Based on preliminary results achieved and reported earlier (41), twelve partition columns with T.C.P. as the stationary liquid were prepared. The tri-meta-cresyl phosphate was dissolved in ethyl ether or in carbon tetrachloride and coated on C-22 firebrick in a ratio of 40:100 to the inert support. In the majority of the cases, a short length of adsorbent was added to improve the separation of gaseous components. The columns varied from 6 to 270 ins as shown in Table VII, which lists the physical characteristics of the twelve columns.

TABLE VII

Description of Various "T.C.P." Columns

Column Number	Type of Column	Mesh size of Inert Solid	Column Modification	Column Length (in)
13	T.C.P. on C-22	18	None	72
21	T.C.P. on C-22	35	None	6 to 18
19	T.C.P. on bentonite	25	None	105
25	T.C.P. on C-22	28-48	None	270
8	T.C.P. on C-22	18	1/4 in charcoal (a)	72
20	T.C.P. on C-22	18-35	4-3/4 in charcoal	72 to 148
22	T.C.P. on C-22	35	Variable in of charcoal	144
14	T.C.P. on C-22	25	1/4 in silica gel (a)	108
17	T.C.P. on C-22	25	1.0 in silica gel (a)	108
15	T.C.P. on C-22	25	2-1/4 in silica gel (a)	108
16	T.C.P. on C-22	25	2-1/4 in silica gel and 1.0 in charcoal (a)	108
18	T.C.P. on bentonite	25	1/4 in silica gel (a)	105

(a) At entrance to column.

Those columns without the addition of short lengths of adsorbent (Column Nos. 13, 21, 19) showed only a poor separation between CH_4 and CO_2. Partial separation was achieved only after extending the column length to 270 inches (Column 25). Separation between N_2 and CH_4 was hardly distinguishable even at this column length. However, the separation between CO_2 and H_2S was complete for even shorter column lengths.

The addition of 1/4 to 4-3/4 in charcoal (35 mesh) at the entrance of the T.C.P. column achieved an improved separation between N_2, CH_4 and CO_2. However, ammonia was irreversibly adsorbed, and the CO_2 and H_2S tailed more than that observed with plain T.C.P. coated columns. These results were ascribed to the action of the short charcoal column.

The addition of short lengths (from 1/4 in to 2-1/4 in) of silica gel to a 9 ft T.C.P. column showed that best separation between CH_4 and CO_2 is achieved with 1.0 in of this adsorption medium. No advantages were gained from either the combination of 2-1/4 in silica gel and 1.0 in charcoal with T.C.P. coated on C-22 firebrick or from 1/4 in silica gel added to 9 ft of T.C.P. coated on bentonite.

(4) Glycerine: Four columns with glycerine coated on C-22 firebrick, 35-50 mesh, in the ratio of 40:100 by weight, varying from 4 to 12 feet in length, were studied. The 4-ft column was unable to separate between N_2, CH_4 and CO_2. With a 6-ft column some slight improvement was noted. As the length was increased to 12-ft, excessive tailing, even for CH_4, made this column unsuitable for analysis.

(5) Stearic Acid: A 6-ft column with a weight ratio of 40:100 stearic acid to inert support (C-22 firebrick 35-50 mesh) was made. The degree of separation achieved between N_2, CH_4 and CO_2 was so small (elution times were found to be 3.62, 3.7 and 3.84 min, respectively, at a flow rate of 22 ml/min) that no further work was done with this column.

(6) Tri-iso-butylene:[19] Two columns, 30 ft and 67 ft long, were studied. Both columns were packed with 28-48 mesh C-22 firebrick, coated with tri-iso-butylene at a ratio of 45:100 liquid to solid. Poor separations between CH_4 and CO_2, and practically no separation between N_2 and CH_4 were obtained.

(7) Tetra-iso-butylene:[20] Since early results appeared very promising, the use of tetra-iso-butylene as a column coating liquid was studied intensively. Ten columns were made and the lengths varied from 78 to 996 inches. All columns were packed with 28 to 48 mesh C-22 firebrick, coated with tetra-iso-butylene at a ratio of 40:100 liquid to solid. While a 210 in long column yielded complete separation between N_2 and H_2S, a 570 in long column was required to separate N_2 from CO_2. A 636 in long column partially separated N_2 and CH_4, and in addition, a small degree of separation between O_2 and N_2 was noticed. The latter was further confirmed by careful measurement of the retention times for O_2 and N_2. These retention data, along with the retention times for hydrogen, methane and carbon dioxide, are listed in Table VIII.

For all the gas-liquid partition columns which had been previously tested, nitrogen and oxygen had the same retention time. This means that these columns could not separate oxygen from nitrogen. However, a small, but distinguishable difference between the retention times of nitrogen and oxygen was noted for this column.

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19 Tri-iso-butylene is manufactured by Eastman Organic Chemicals, a division of Eastman Kodak Company, Rochester 3, New York.

20 Tetra-iso-butylene is manufactured by Eastman Organic Chemicals, a division of Eastman Kodak Company, Rochester 3, New York.

TABLE VIII

Retention Times Measured from a 636-in Tetra-iso-butylene Column (*)

Component	Sample Size (ml)	Retention Time (sec)
H_2	0.1	307.5
H_2	1.0	308.0
N_2	0.1	308.0
N_2	1.0	309.0
O_2	0.1	313.0
O_2	1.0	312.0
CH_4	0.1	349.0
CH_4	1.0	349.0
CO_2	0.1	442.0
CO_2	1.0	441.0

(*) Note: Shorter tetra-iso-butylene columns were known to separate H_2S from the other gas components. Therefore, with this particular column no retention times for H_2S were measured.

There are two other conclusions which may be drawn from the data shown in Table VIII: (a) the column does not separate hydrogen and nitrogen, and (b) up to a sample size of 1.0 ml, the retention time is independent of the sample size.

The column finally selected for the routine analysis was 746 inches long. This column completely separated N_2, CO_2 and H_2S and almost completely separated N_2 from CH_4. At a helium flow rate of 120 ml/min and a column temperature of 78°F, it was found that for the same volume of samples (1.5 ml), the peak height of CH_4 (6.60 units) is almost the same as that for CO_2 (6.79 units). On the other hand, N_2 showed a much higher peak (7.87 units) than that for air (6.20 units), i.e., a peak composed of oxygen and nitrogen. Since the thermal conductivities of oxygen and

nitrogen are almost equal, the lower peak height of air can only be explained by the fact that the chromatogram for air is actually composed of two slightly separated chromatograms, i.e., nitrogen and oxygen. The width of the composite air peak is broader than a single chromatogram of nitrogen and consequently the peak is lower than the peak produced from an equal size sample of nitrogen.

(8) Dimethyl Sulfolane: This liquid coating has been recommended by Keulemans (42) for the separation of light hydrocarbons (C_1 to C_5). A 12-ft column packed with 28 to 48 mesh C-22 particles, coated with dimethyl sulfolane in a ratio of 30:100 (liquid to solid by weight) was studied. It showed a superior separation between CH_4 and CO_2 compared to any of the other gas-liquid partition columns which had been heretofore studied. However, the separation between N_2 and CH_4 was poorer than that obtained from tri-meta-cresyl phosphate and tetra-iso-butylene columns. Because of the relatively high volatility of dimethyl sulfolane, the column could not be operated at a temperature exceeding 100°F. No ethane or higher hydrocarbons were observed in sludge gas with this column.

(9) Squalane: Squalane is a saturated hydrocarbon with a large number of methyl groups (2, 6, 10, 15, 19, 23-hexamethyl tetracosane, or $C_{30}H_{62}$). The formula and boiling points are given in Table V. The theory of solution, according to Hildebrand and Scott (43), states that a saturated hydrocarbon is a favorite solvent for another saturated hydrocarbon. Therefore it was expected that squalane would be a preferred solvent for methane, the first member of the saturated hydrocarbon series. The increase of solubility was expected to improve the separation between nitrogen and methane, provided that the solubility of nitrogen in

squalane would not increase proportionately with that of the CH_4. Experimental results from a 756 in long column packed with squalane-coated C-22 firebrick, 28-48 mesh, with a coating ration of 50:100 (liquid to solid by weight) indicated that the ability of squalane to separate N_2 from CH_4 was comparable with that achieved by tetra-iso-butylene. However, squalane did not show any separation between oxygen and nitrogen, whereas the tetra-iso-butylene did. The squalane column also gave poorer separation between CH_4 and CO_2 than that obtained by the tetra-iso-butylene column since the separation was complete with the latter column but a slight overlapping resulted when the former column was employed. The squalane column completely separated CO_2 from H_2S, although the distance between CO_2 and H_2S peaks was less than that obtained with the tetra-iso-butylene column.

Another squalane column was packed with 28-48 mesh C-22 firebrick particles and a coating ratio of 30:100 liquid to solid into a 1080 in long and 1/8 in I.D. polyethylene tube. This column was connected in series with the 756 in column just discussed. The combined column produced a wider separation between N_2, CH_4 and CO_2 peaks. However, because of the strong longitudinal diffusion effect of a column of such length, the lower portion of the three peaks - close to the base line - still overlapped slightly. The results prove that complete separation cannot be achieved by simply increasing the length of a column.

The squalane column did not temporarily retain, nor irreversibly adsorb, ammonia. Ammonia samples were eluted from the column with the same speed as nitrogen.

There can be three conditions imposed on a sample injected into a column for gas chromatographic separation into its individual components:

(a) the component is temporarily retained, giving rise to separation and identification;

(b) irreversible adsorption, the sample is permanently adsorbed; and

(c) the sample is eluted at the same rate of speed as carrier gas which will show no separation.

For the squalane column, CH_4 and CO_2 follow case (a), H_2S follows case (b), and nitrogen follows case (c).

(10) Silicone Oil 550: The resolving power of silicone oil 550[21] liquid coating was found to be comparable with that of silicone grease. The former was better for the separation of N_2 from CO_2 but was slightly poorer for the separation of N_2 from CH_4. The quality of resolution between CH_4 and CO_2 was equal for both liquids.

The irreversible adsorption of H_2S which occurred in the silicone oil column, as well as in the other columns described heretofore, was studied intensively for this particular column. A total of twenty columns, coated with silicone oil 550, were prepared to investigate the effects of: (a) varying coating ratio and (b) pre-treatment of solid supporting material on irreversible adsorption. The details of this study are presented in Chapter 6, Section B, "The Analysis of Hydrogen Sulfide."

(11) Triton X-100:[22] This solvent exhibited the greatest resolving power toward the separation between CO_2 and H_2S, compared to all other partition liquids mentioned. The separation between CH_4 and CO_2 is also

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21 Silicone Oil 550 is manufactured by Dow Corning Corp., Midland, Mich.

22 Triton X-100 is manufactured by Rohm and Haas, Philadelphia 5, Penna.

slightly improved over that achieved by squalane and silicone oil 550. The major disadvantage of Triton X-100 is that it cannot separate N_2 from CH_4.

Summary of Experimental Results and Conclusions

In order to compare the resolving power of the stationary phases, i.e., both solid adsorbents and partition liquids, on a quantitative basis, the specific retention volume of sludge gas constituents in the stationary phases of columns which resolved two or more components of sludge gas, are presented in Table IX.

TABLE IX

Specific Retention Volume for Sludge Gas Components Eluted from Solid and Liquid Adsorbents

Column Adsorbent	Specific Retention Volume, V^o_g, ml/gm					
	O_2	N_2	CH_4	CO_2	H_2S	NH_3
Molecular Sieve 5A	1.00* (75°F)	3.17* (75°F)	4.84* (75°F)	+	+	+
Molecular Sieve 13X	2.75 (75°F)	7.42 (75°F)	14.35 (75°F)	+	+	+
Silica Gel	**	**	0.0514* (130°F)	1.0* (130°F)	+	+
Tetra-iso-butylene	0.054 (77°F)	**	0.399 (75°F) 0.422 (83°F)	1.51 (75°F) 1.30 (83°F)	5.23 (75°F)	26.93 (75°F) +
Tri-iso-butylene	**	**	**	0.215 (70°F)	-	+
Silicone Oil 550	**	**	0.264 (82°F) 0.256 (90°F) 0.246 (140°F)	1.16 (82°F) 1.13 (90°F) 0.877 (140°F)	6.34 (83°F) 5.47 (90°F) 3.95 (140°F)	+ + +
Silicone Grease	**	**	0.314 (73°F)	1.03 (73°F)	4.63 (73°F)	+
Squalane	**	**	0.381 (80°F) 0.318 (90°F) 0.235 (141°F)	1.12 (80°F) 0.960 (90°F) 0.627 (141°F)	4.98 (80°F) 4.09 (90°F) 2.61 (141°F)	+ + +
Tri-meta-cresyl-phosphate	**	**	**	0.484 (80°F)	3.77 (80°F)	+
Dimethyl Sulfolane	**	**	0.074 (73°F)	3.33 (73°F)	-	+
Triton X-100	**	**	**	1.25 (91°F)	9.67 (91°F)	+

* These values are only relative retention volumes, referred to V^o_g for O_2 or CO_2 as 1.0. No absolute value can be calculated because in the early stage of these investigations the weight of adsorbent packed into the column was not determined.

** No separation between the component and inert carrier gas.

\+ The component is being adsorbed irreversibly.

Chapter 5

DETERMINATION OF OPTIMUM OPERATING CONDITIONS

A. Effect of Flow Rate

According to Van Deemter's (44) theory, column efficiency is a function of the linear flow rate of carrier gas inside a chromatographic column. Theoretically, there is an optimum flow rate at which the column performs most efficiently. However, due to the compressibility of the carrier gas, the linear velocity of carrier gas across a column is not uniform. An increase in the flow rate is always accompanied by an increase of pressure drop across the column. The pressure gradient creates the correspondent linear velocity gradient across the column. To optimize the linear velocity along a selected section of a column may force the linear velocity in the other sections of the column to become too high or too low to be optimum. Therefore, the overall effect of optimization is diminished for a long column when a large pressure gradient exists across the column.

To illustrate, the column efficiency, expressed as the number of theoretical plates, of a 35-ft column appears to be fairly independent of the flow rate in the range of 32 ml/min to 140 ml/min as shown by the experimental data presented in Table X. For a short, (4-3/4 ft) column, with a small pressure gradient, column efficiency increased with the increase of flow rate.

The concentration of sample gas in the elution stream is inversely proportional to the flow rate. Therefore, a constant flow rate is one of the most essential factors to achieve reproducible results for quantitative analysis. Within limits, higher flow rates give sharper peaks, i.e., greater E_{max} : w ratio, (where E_{max} is the peak height and

TABLE X

Plate Number Versus Flow Rate

Column: 35 ft silicone grease column
Solid support: 28-48 mesh C-22 firebrick
Temperature: 75°F

Flow Rate	N_{CH_4}	N_{CO_2}	N_{H_2S}
32 ml/min	672	-	1710
89 ml/min	686	490	1135
140 ml/min	495	560	1367

Column: 4-3/4 ft silicone grease column with 3-in charcoal at exit
Solid support: 28-48 mesh C-22 firebrick
Temperature: 76°F

Flow Rate	N_{CH_4}	N_{CO_2}	N_{H_2S}
42 ml/min	64	57	25
75 ml/min	80	60	28
89 ml/min	94	74	42

w is the peak width), and also tailing[23] is reduced. A higher flow rate decreases the retention time and the analysis time, but does not affect the retention volume. Therefore, higher flow rate is in general preferred, provided it will not dilute the sample too far to reduce the sensitivity of the detection system and create an excessive pressure drop across the column. A flow rate of 70 ml/min to 100 ml/min was found to be a practical range for analysis.

B. Effect of Column Temperature

The retention volume of a given column is quite sensitive to the column temperature. In general, the adsorption power of most solid or liquid adsorbents toward gases decreases sharply as temperature increases. Therefore, increasing the temperature reduces the retention volume, and consequently the resolving power.

For example, a 6-ft molecular sieve 13X column separates oxygen and nitrogen at 75°F, but completely loses its resolving power for these two gases at 169°F. N_2 and CH_4 may be separated by a 12-ft silica gel column at 70°F but the separation becomes very poor at 150°F. On the other hand, an increase in temperature will sharpen the chromatogram and reduce tailing. Since the number of plates is calculated as the ratio of retention time and width of chromatogram, it should be noted that generally the temperature has less effect on the number of plates than the retention volume of a column. Several examples of varying the column temperature are listed in Table XI.

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23 "Tailing" of a component in gas chromatographic analysis is a common term referring to an unsymmetrical tail of the normal binomial distribution curve of chromatogram peak.

TABLE XI

Effect of Temperature on Retention Volume and Number of Plates

Column: 6-ft molecular sieves 13X, 14-28 mesh
Carrier gas: Helium

Temp.	Flow Rate	O_2		N_2		CH_4	
		Retention Volume	Number of Plates	Retention Volume	Number of Plates	Retention Volume	Number of Plates
76°F	72 ml/min	88	537	110	390	191	337
160°F	102 ml/min	(*)	(*)	104	304	128	196

(*) O_2 can no longer be separated from N_2

Column: 12-ft silica gel, 28-48 mesh
Carrier gas: Helium

Temp.	Flow Rate	N_2		CH_4		CO_2	
		Retention Volume	Number of Plates	Retention Volume	Number of Plates	Retention Volume	Number of Plates
76°F	91 ml/min	109	114	179	162	1710	155
130°F	80 ml/min	120	376	132	152	550	165

Column: 12-ft silicone grease on C-22 firebrick, 28-48 mesh, ratio of liquid to solid 60:100 by weight
Carrier gas: Helium

Temp.	Flow Rate		N_2		CO_2	
			Retention Volume	Number of Plates	Retention Volume	Number of Plates
65°F	80 ml/min		72	177	99	242
59°F	80 ml/min		75	184	108	167
37°F	80 ml/min		83	190	120	207

Note: 12-foot silicone grease column was too short to separate CH_4 from N_2.

C. Comparison of Plate Efficiency of Various Columns

As the result of considerable experimental work, Table XII has been prepared to summarize the data and calculated parameters, which include the plate efficiency of various columns, expressed as number of theoretical plates, N; height equivalent to a theoretical plate, H.E.T.P.; separation factor, R; and separation factor per unit length of the column R/L. Only those columns which showed satisfactory separation between at least two components of sludge gas were listed.

To study the effect of water vapor in sludge gas samples on a 12-ft silica gel solid adsorption column, the column efficiency of this particular column was studied over a period of sixty days with approximately twenty samples analyzed per day. The samples of sludge gas were saturated with water vapor at room temperature. The plate numbers, calculated from only those data obtained, H.E.T.P. and separation factors, every fifth day, are listed in Table XII. It appears that the efficiency of the column did not decrease, but slightly increased with time, as indicated by the general increase of the number of plates, N, decrease of the H.E.T.P. and increase of the separation factor, R.

As has been mentioned previously, a separation factor greater than 1.5 is taken as the criterion of complete separation. From Table XII, it is seen that all the columns listed separated H_2S from N_2 completely, except the 6-ft Triton X-100 column at 194°F and the 29-ft silicone oil 550 column at 133°F. It was found that the 12-ft silica gel column adsorbed H_2S irreversibly, thus no separation data could be obtained. Silicone grease, tetra-iso-butylene, and silica gel columns separated CO_2 from N_2 completely. For the separation between N_2 and CH_4 none of these columns

TABLE XII

Comparison of Plate Efficiency of Various Columns at Different Operating Conditions

Adsorbent or Partition Liquid	Column Length (ft)	Column Temp. (^{o}F)	Column Inlet Pressure (psig)	N_{CH_4} $\bar{x}\pm\sigma$	N_{CO_2} $\bar{x}\pm\sigma$	$HETP_{CH_4}$ $\bar{x}\pm\sigma$	$HETP_{CO_2}$ $\bar{x}\pm\sigma$	Separation factor between N_2 and CH_4 $\bar{x}\pm\sigma$	Separation factor per unit length between N_2 and CH_4 $\bar{x}\pm\sigma$	Separation factor between N_2 and CO_2 $\bar{x}\pm\sigma$	Separation factor per unit length between N_2 and CO_2 $\bar{x}\pm\sigma$	Separation factor between N_2 and H_2S $\bar{x}\pm\sigma$	Separation factor per unit length between N_2 and H_2S $\bar{x}\pm\sigma$
Silicone grease	81	73	50	3007±124	2525±643	.0269±.0011	.0321±.0082	.917±.044	.0113±.0054	3.40±.05	.0420±.0006		
" "	71	79	30	2629±306	2828±339	.0270±.0031	.0251±.0030	.674±.118	.0095±.0017	3.19±.17	.0449±.0024		
" "	71	86	20	3767±454	3173±298	.0188±.0019	.0224±.0021	1.003±.239	.0141±.0034	3.33±.25	.0469±.0035	7.90*	0.111*
" "	71	87	25	2853±496	3269±214	.0249±.0043	.0217±.0014	.913±.086	.0129±.0012	3.37±.19	.0475±.0027		
" "	71	86	30	2434±252	2694±234	.0292±.0030	.0240±.0019	.791±.116	.0111±.0016	3.09±.30	.0435±.0042		
Tetraisobutylene	25-1/4	83	20	-	508±23	-	.0497±.0022	-		1.02±.02	.0404±.0008		
"	25-1/4	83	40	-	944±80	-	.0267±.0023	-		1.34±.16	.0531±.0064		
"	30	73	20	637±4	1071±67	.0471±.0003	.0280±.0018	.652±.014	.0217±.0005			6.49±.11	.216±.004
"	30	75	20	713*	959±108	.0421*	.0313±.0035	.647*	.0216*	2.38±.15	.0793±.0050		
"	30	73	30	967±36	1171±111	.0310±.0011	.0256±.0024	.768±.090	.0256±.0030	2.44±.10	.0813±.0033		
"	39-3/4	83	50	-	1854*	-	.0214*	.715±.010	.0180±.0003	-	-		
"	39-3/4	83	60	-	1782±0	-	.0223±0	.737±.000	.0185±.0000	2.47±.01	.0621±.0003		
Silica Gel	12	130	5	188±11	198±9	.0638±.0038	.0606±.0027	.598±.045	.0498±.0038	4.76±.15	.397±.013		
" "	12	130	5	163±18	173±7	.0736±.0081	.0694±.0028	.529±.078	.0441±.0065	4.43±.13	.369±.011		
" "	12	130	5	175±5	163±3	.0686±.0020	.0736±.0013	.508±.087	.0423±.0073	4.19±.05	.349±.004		
" "	12	130	5	218±25	199±8	.0550±.0063	.0603±.0024	.667±.067	.0564±.0056	4.75±.15	.396±.013		
" "	12	130	5	226±18	224±23	.0531±.0042	.0536±.0055	.766±.058	.0638±.0048	4.93±.25	.411±.021		
" "	12	130	5	264±10	327±8	.0455±.0017	.0367±.0009	.796±.057	.0663±.0048	4.97±.16	.414±.013		
" "	12	130	5	216±22	213±35	.0556±.0057	.0563±.0092	.813±.201	.0678±.0168	5.03±.03	.419±.003		
" "	12	130	5	246±21	221±8	.0488±.0041	.0543±.0020						
Triton X-100	6	86	20	Could not	67±7		.0896±.0094					2.47±.01	.413±.002
" "	6	88	20	separate	-		-					2.56±.13	.427±.022
" "	6	86	30	CH_4 from N_2	85±1		.0706±.0008			.539±.030	.0898±.0050	2.41±.10	.403±.017
" "	6	140	20		-		-					1.44±.05	.240±.008
" "	6	194	20		-		-					0.585**	0.097**
Triton X-305	6	93	15		25±3		.240±.029			.317±.037	.0528±.0062	2.04±.08	.340±.013
Aerosol OT	14	93	20		54±4		.259±.019			.503±.080	.0359±.0057		
"	14	135	20									1.08±.04	.077±.003
Silicone Oil 550	29	133	20		265±41		.109±.017			.830±.014	.0286±.0048	4.23±.41	.146±.014

* - Reference to single value.

** - In this column the particles of Fluoropak were used as the solid support. In all the other columns Firebrick C-22 particles 28-48 mesh were used.

listed has a separation factor greater than 1.5. However, the separation factor of the 71-ft silicone grease column is greater than 1.0 at a temperature of 86°F and 20 psi inlet column pressure. The separation of N_2 and CH_4 by this column was nearly complete, with only slight overlapping which did not affect the accuracy of the analysis, when the peak height of the chromatograms were measured and the amount of N_2 present was less than 20%. The N_2 content in sludge gas is generally considerably less than 20%.

Chapter 6

SPECIAL PROBLEMS ENCOUNTERED IN THE ANALYSIS OF MINOR COMPONENTS

The composition of the sludge gas depends on the source of the sludge (sewage and/or trade wastes) and the condition of the digestion process. Based on the daily gas analyses from over twenty experimental digestion runs, each with 16 to 18 digesters, covering a period of three years, it has become quite evident that CH_4, CO_2, N_2, O_2 and argon make up at least 98% of the sludge gas. The remaining part, if any, may be H_2 and H_2S. Both of these gases have been reported from time to time as present in samples of digester gas under certain conditions from various sources (45)(46)(47). These minor components, which may be analyzed readily if they exist in sizeable concentrations, present a difficult challenge to gas chromatographic analysis, especially in concentrations of the order of several hundred parts per million or less. The special problems encountered in the analysis of minor components and their solutions are discussed in the separate sections to follow:

A. The Analysis of Hydrogen

There is some question of whether or not hydrogen is ever present in sludge gas produced from the decomposition of domestic sewage. It is certain that some hydrogen will be produced from a fermentation process when the pH of the solution is low and a high percentage of hydrogen acceptors abound in the digesting medium. During two special digestion runs carried out in the laboratory, the digester bottles were filled with glucose and seeded with digested sludge, instead of starting with raw domestic sludge. As a result, it was found that 20% of the gas produced was

hydrogen[24]. Occasionally, a small percentage of hydrogen gas has been casually cited in the literature (45)(46). However, these analyses were conducted by the conventional Orsat method in which the quantity, or concentration, of hydrogen gas was presumably obtained only indirectly by

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[24]The data of 20% H_2 by volume was not obtained by direct measurement. Instead, it was obtained from the difference of sample volume injected and the summation of the volumes of N_2, CH_4 and CO_2 calculated from their respective chromatograms. Since helium was employed as the carrier gas and the thermal conductivities of hydrogen and helium are known to be very close to each other, the thermal conductivity detector is not sensitive to the hydrogen gas. The presence of 20% hydrogen gas would only produce a very small peak which the 12-ft silica gel column could not distinguish from the N_2 peak. Therefore, the hydrogen gas "disappeared" from the chromatogram. It is reasonable to assume that the volume disappeared was hydrogen because it is known that all the gases, other than hydrogen and helium, are sensitive to the thermal conductivity detector. Fermentation processes do not release helium. One possible error is the presence of H_2S or NH_3 in the sample because both gases are irreversibly adsorbed by silica gel columns. This error would be small because the concentrations of NH_3 and H_2S were low, if at all present in the fermentation gas.

The presence of a high concentration of hydrogen in the gas produced from the fermentation of glucose was confirmed in later experiments in which the glucose solution was seeded with a pure E. Coli culture. The composition of the gas was found to be 50% CO_2 and 50% hydrogen by volume. This ratio agrees with the results reported in Bergey's Manual (48).

The composition of the digester gas was analyzed with a 12-ft molecular sieve column for hydrogen and a 61-ft tetra-iso-butylene column for N_2, CH_4 and CO_2. The analysis by the molecular sieve column used nitrogen as the carrier gas. No methane was found during the six day period. Some of the results are shown below:

Relative Volumes of H_2 and CO_2 from the Fermentation of Glucose by E. Coli

Date	Time	Relative Volumes	
		Hydrogen	Carbon Dioxide
Feb. 6, 1959	10:30 AM	1.08	1.09
Feb. 6, 1959	5:00 PM	1.04	0.89
Feb. 9, 1959	5:00 PM	0.49	0.51
Feb. 10, 1959	5:30 PM	0.30	0.33
Feb. 11, 1959	6:00 PM	0.24	0.23

difference. Therefore, an unaccountable volume of sample gas may have been erroneously reported as hydrogen. In the work carried out in our laboratory, no hydrogen was detected in the gas produced from sludges from two Atlanta, Georgia, sewage treatment plants[25].

Only molecular sieve columns, types 5A and 13X, were found to be satisfactory for the separation of hydrogen from nitrogen and oxygen. Silica gel and activated charcoal adsorbents have also been used by some workers (49), however, their reported performance is inferior to that obtained by molecular sieves.

In the analysis of hydrogen, nitrogen instead of helium was used as the carrier gas. This was necessary because of the small difference between the thermal conductivities of hydrogen and helium which made the thermal conductivity cell very insensitive to the detection of hydrogen. The restriction to nitrogen carrier gas required the performance of a separate analysis run, or to use a separate unit to analyze for hydrogen, while the remaining components were analyzed in the usual manner, using helium as the carrier gas. When nitrogen was used as the carrier gas, the thermal conductivity cell sensitivity for hydrogen was high (See Appendix I, "Sensitivity of Thermal Conductivity Cells"). Hydrogen was detected in concentrations as low as 100 ppm by a molecular sieve 5A or 13X column in the presence of oxygen and nitrogen.

When helium was used as the carrier gas, a thermal conductivity cell[26] was capable of detecting hydrogen only if the concentration of hydrogen in the

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[25] Both primary and seed sludges were obtained from two local plants. The Clayton plant has a 60 mgd capacity and has primary treatment only. The Flint River plant contains complete biochemical oxidation and is well operated with a design flow capacity of 8 mgd. Both treatment plants receive predominantly domestic sewage, one of the major reasons for employing their sludges as the experimental substrate throughout the studies reported herein.

[26] Model NRS or 30S tungsten filament wire cells, manufactured by the Gow-Mac Instrument Co., 100 Kings Road, Madison, New Jersey.

sample was relatively high, i.e., greater than ten per cent. However, in respect to the hydrogen concentration, the response of the thermal conductivity cell was not linear. In the presence of a small amount of hydrogen (less than 1 ml), the hydrogen chromatogram appeared as a small positive peak. An increase in the size of the hydrogen sample inverted the peak to the negative side of the base line. Consequently, the recorder chart showed a positive peak, an inverted or negative peak and followed by another positive peak, as shown in Figure 8-5. This phenomenon, which has been observed in the He-H_2 system, but not in the N_2-H_2 system, makes the quantitative interpretation of the hydrogen concentration peak difficult when helium is used as the carrier gas.

The phenomenon of "inverted" peaks observed in the He-H_2 system indicates that the relation between thermal conductivity and hydrogen concentration on the He-H_2 system is not linear. Although the thermal conductivity for pure hydrogen is greater than pure helium, the relation between the thermal conductivity and concentration of hydrogen for a He-H_2 mixture initially decreases, goes through a minimum, and then increases in the higher hydrogen concentration range. Therefore, the presence of the hydrogen sample appears as a positive peak. A large H_2 sample eluting from the gas chromatographic column consists of a dilute concentration front, a middle portion of the higher concentration, and followed by the tail of another dilute hydrogen concentration. Therefore, the chromatogram consists of a small positive peak, a negative peak and another small positive peak.

B. The Analysis of Hydrogen Sulfide

Sludge gas may contain hydrogen sulfide up to several hundred ppm, as pointed out by Babbitt (2) and Buswell (50), depending on the condition, age and origin of the digesting medium. The analysis of hydrogen sulfide imposes a special problem to the gas chromatographic method. Unlike methane, which is difficult to separate from nitrogen, the separation of hydrogen sulfide from the other major components of sludge gas (nitrogen, methane and carbon dioxide) is relatively easily achieved. Many partition liquids, such as silicone grease, silicone oil 550, tri-iso-butylene, squalane, and Triton X-100 give satisfactory results. Among these partition liquids, Triton X-100 has the greatest specific retention volume, i.e., 9.67 ml/gm at 91°F, which compares with 4.63 ml/gm at 73°F for silicone grease columns, 5.47 ml/gm at 90°F for silicone oil 550 columns, 5.23 ml/gm at 75°F for a tetra-iso-butylene column and 4.09 ml/gm at 90°F for a squalane column, as shown in Table IX.

The major problem encountered in the gas chromatographic analysis of hydrogen sulfide was its irreversible adsorption by the column material. To illustrate, a small size sample of hydrogen sulfide would not pass through a gas-liquid partition column unless the column packing was saturated previously by a hydrogen sulfide sample (approximately one ml was adequate). The prior saturation requirement is especially important for columns made of copper tubing, as hydrogen sulfide reacts with copper at normal temperature. Replacing the copper with polyethylene tubing reduced the irreversible adsorption to a minimum. In one of the experiments, a sample as small as 0.0007 ml H_2S (0.9 ml air-H_2S mixture containing 812 ppm H_2S by volume) passed through 27 feet of polyethylene tubing packed with silicone oil 550 coated on C-22 firebrick, and produced a peak signal of 0.014 mv. However,

subsequent H_2S samples of identical size produced a peak of 0.027 mv. This method of procedure was used to prove that the first sample has been partially adsorbed. From a carefully designed analysis of various samples with different liquid to solid ratios, it was determined that the permanent adsorption capacity of the column decreased with an increase of the liquid-solid ratio. Therefore, it appears that the irreversible adsorption is caused by the solid support (firebrick, Celite, etc.) rather than by the coating liquid.

The undesirable irreversible adsorptivity of the solid support has been the subject of considerable discussion by Knight (51), Kwantes (52), and Johns (53), who investigated different solid support materials and concluded that C-22 firebrick solids possess the least adsorptivity. Ciola (54) observed that firebrick particles should be pretreated by washing them with an acid solution. Similar treatment with dil. HCl (aq. solution) to confirm this observation, did not offer promising results for the analysis of hydrogen sulfide. Various methods of de-activation of firebrick and Celite were investigated at this laboratory. The procedures applied included: (a) washing with an alkali solution, such as dil. sodium hydroxide; (b) washing with an inorganic acid, such as concentrated or dil. hydrochloric acid; (c) precoating with an organic compound, such as stearic acid, oleic acid or glycerine, (d) mixing the organic compound with the partition liquid (the latter included Silicone Oil 550 and tri-ethylene glycol). In several instances even combinations of the above methods were employed when it appeared to be advantageous.

The best results were obtained by the following treatment procedure: To a suspension of 200 gm, 28-48 mesh, C-22 firebrick in 500 ml distilled water, add 20 ml of 0.1 N NaOH (aq. solution) to bring the pH to 10.5. Discard the strongly basic solution and rinse the firebrick with distilled

water until its pH reached 7.3. Dry the firebrick solids in a 600°F oven for one hour, then precoat the firebrick with stearic acid (3% by weight of the firebrick) before coating it with a partition liquid, such as silicone oil 550, tetra-iso-butylene, etc.

A comparison of the adsorptivity of various solid support materials was made. Several materials were coated with silicone oil 550. Of these, Celite 545 appeared to have a greater adsorptivity than firebrick C-22, although uncoated solid particles showed the opposite effect, i.e., the uncoated C-22 firebrick separated H_2S from N_2, while Celite 545 did not. Alundum, studied as another solid support material, was found to have a low adsorptivity. A column packed with silicone oil-coated alundum solids permitted H_2S to pass through readily, even for small size samples. However, the column lost its ability to separate nitrogen from H_2S after several sample injections and nitrogen and H_2S were eluted from the column simultaneously showing a single peak. It was recognized that Fluoropak[27] is also an excellent inert column solid support material. It was established that it has negligible adsorption toward H_2S; however, the efficiency for the packed column was found to be low. In a comparison between two columns, one packed with C-22 firebrick, the other with Fluoropak, and both coated with Triton X-100, the separation factors between N_2 and H_2S per unit length, $R_{1.4/L}$, were found to be 0.427 and 0.0097, respectively.

The basic problem in the analysis of H_2S in sludge digestion gas is the low concentration involved. The adsorption phenomenon will introduce little difficulty during the analysis of a sample containing H_2S if its

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[27] Fluoropak 80, a trade name for Teflon powder manufactured by the Fluorocarbon Co., 1206 E. Ash Ave., Fullerton, California.

volume is greater than 0.01 ml. In addition, non-corrosive tubing, such as polyethylene, is required for the column, because the adsorptive capacity of the solid support is small and it can be saturated easily. A quantity of 0.01 ml H_2S corresponds to a concentration of 10,000 ppm of H_2S in a 1.0 ml size sludge gas sample. This concentration is greater than would normally be expected in domestic sewage sludge gas. The problem can not be solved by merely using a larger sample size. A sample size greater than 10 ml significantly reduces the column efficiency.

To detect H_2S in the hundred ppm range requires a sensitive detector and recorder. In a four element tungsten-wire, thermal filament type conductivity cell, a 0.001 ml sample of H_2S can produce only a signal of 0.004 mv (at a helium carrier flow rate of 92 ml/min, at room temperature, and with a filament current of 200 ma). Therefore, to be able to analyze a sludge digestion gas sample containing 100 ppm H_2S, it was necessary to use a 10 ml size sample to produce a peak of only four per cent of full chart scale on a one millivolt (full range) recorder.

To amplify the output signal of the detector, a Keithley[28], Model 150 AR, high gain microvoltmeter was used as an amplifier in conjunction with a Wheelco strip-chart recorder to attain a sensitivity of 100 μv full scale. However, the increase of the background noise level neutralized the advantage gained from signal amplification.

In the usual routine of domestic sewage treatment plant operation, information on the H_2S concentration in the sludge gas may not be as important as that of CO_2 content. In those cases where an accurate H_2S content of the sludge gas is desired, the gas chromatographic method may be employed successfully with the following precautions:

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[28] Keithley, Model 150 AR, manufactured by Keithley Instruments, 12415 Euclid Ave., Cleveland, Ohio.

1. The chromatographic column should be composed of a non-corrosive tubing, such as polyethylene, Teflon, or stainless steel.

2. The irreversible adsorption of the column is proportional to the amount of the solid support present. Therefore, the minimum column length should be employed, sufficient for the complete separation of H_2S from the adjacent component, namely CO_2. In this respect, Triton X-100 is a better partition coating liquid than silicone oil 550. When Triton X-100 is used as the partition liquid, only about half the column length is necessary to achieve complete separation of H_2S and CO_2. Triton X-100 coating on Fluoropak is considered an optimum partition column combination for the separation of H_2S from sludge digestion gas.

3. For the complete resolution of a sluge gas sample into all four components, i.e., N_2, CH_4, CO_2 and H_2S, an additional length of column, longer than that required to separate CO_2 and H_2S, is needed. In this case Fluoropak is not recommended as the solid support material because an excessive length of column would be required due to the low efficiency of Fluoropak. Instead, firebrick C-22 is recommended as the stationary support material.

4. It is advisable to pre-saturate the column by injecting a relatively large H_2S sample (say, 0.5 ml of H_2S) before each analysis to overcome irreversible adsorption. The injection of a few sludge gas samples containing H_2S, prior to the start of the analysis, is also effective and a recommended procedure.

Chapter 7

EXPERIMENTAL PROCEDURES FOR SLUDGE DIGESTION GAS ANALYSIS

In this chapter the details of the experimental procedures, including column preparation, sampling and interpretation of the chromatogram are described.

A. Preparation of a Gas-Liquid Partition Column

(1) Solid Support: Of the many solid support materials studied, C-22 firebrick was found to be the best general purpose solid support, also was proven to have the highest plate efficiency. To prepare the solid support, the firebrick was first ground; graded by sieve screens to the desired particle size, 28-48 mesh; washed with distilled water to remove fine particles and dust, followed by drying in a 300°C oven for one and one-half hours. The dried particles were stored inside a desiccator before coating.

(2) Liquid-Coating: A quantity of coating liquid, corresponding to 40 parts liquid to 100 parts solid, by weight, of the firebrick particles, was dissolved in a volatile solvent. Ether was generally the best choice, added in sufficient quantity to make the total volume of the solution approximately the same as the apparent volume of the firebrick particles. The firebrick particles were submerged in the solution and stirred thoroughly. After a period of ten minutes, sufficient to provide adequate contact, the coated particles were spread on an open tray and allowed to dry at room temperature.

(3) Packing of the Column: A definite length of plastic, or stainless steel tubing, of 1/8-in to 1/4-in I.D. was packed by blocking one end and pouring the coated particles into the open end through a funnel. It

was essential to shake and tap the tubing vigorously to assure that the column was uniformly packed. From experience, three grams of coated particles, 28 to 48 mesh, packed into each foot of 3/16 in I.D. copper or stainless steel tubing, whereas about 1.7 gms could be packed into each foot of 1/8 in I.D. plastic tubing. When the required column length exceeded 12 feet, it became necessary to pack the column in sections, joined together by unions. The column ends were sealed with a glass wool plug. The column was placed into the column oven compartment to equilibrate at the temperature selected for its operation.

B. Preparation of Gas-Solid Adsorption Column

An adsorption column was prepared by grinding a solid adsorbent and screening out the 28-48 mesh portion. The selected portion was dried in a 300°C oven for one and one-half hours, and packed in the same manner as a partition column.

C. Collection of Gas Sample for Analysis

Sludge gas samples were collected from inside 4-liter glass bottle digesters, as close as possible to the digesting sludge to assure the collection of representative samples. To remove a sample from a laboratory digestion bottle, a glass tee was inserted through the stopper of the glass bottle with one end of the tee covered by a rubber serum cap. The third end of the tee went to a gasometer. The gas sample was withdrawn from the digester through the serum cap by a syringe.

The size of sample required for quantitative analysis was found to depend on the voltage measuring range of the recorder. When using an automatic recorder with a 0 to 1 mv range, a 0.1 ml sample was sufficient, but a 0.5 to 1.0 ml volume of gas sample was required if a 1 to 10 mv full

range recorder was used. Among the various types of sampling devices available, a hypodermic syringe was used for the injection of the gaseous samples. For sample sizes greater than 0.1 ml the hypodermic syringe was used. For smaller size samples, a Teflon tipped, gas-tight microsyringe[29] with a total capacity of 0.1 ml has recently become available. Before each sampling, the syringe was flushed several times with the sample gas. When transfer of the sample over a relatively long distance was necessary, the needle of the sample syringe was inserted into a rubber stopper to prevent leakage.

During automatic analysis, the samples were injected into the chromatographic column by an automatic sampling valve, shown in Figure 5, according to a predetermined time schedule.

D. Operational Procedures of Gas Chromatographic Analysis

The performance of gas chromatographic analysis is simple, provided the necessary equipment is available. To illustrate, the individual steps which were followed during this study to carry out an analysis are outlined briefly below:

1. The valve of a helium gas tank was opened to let the carrier gas flush out any air which had diffused into the chromatographic column since the last analysis. The two-stage proessure gauge was adjusted to the desirable pressure to maintain a constant flow rate, usually at approximately 60 ml/min.

2. The heater of the column oven and the current for the detector were then turned on and adjusted to the desired value.

3. The rubber serum cap over the sample injection point was checked against leakage by soap solution and replaced if any gas leakage

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[29] Microsyringe, Model GS-1710, a product of the Hamilton Company, Whittier, California.

was found. Ordinarily, a serum cap could withstand 200 to 300 sample injections, depending on the needle gauge used.

4. The recorder was turned on approximately 30 minutes after the helium gas valve was opened. The base line on the recorder chart was adjusted to zero. The analysis could be started after a stable base line was obtained.

5. Sludge gas usually contained three components: Nitrogen (predominantly introduced from air leaks into the digester or during sampling), CH_4 and CO_2. Approximately ten minutes after sample injection, nitrogen appeared as the first peak on the recorder when a 71-ft gas-liquid partition (silicone grease) column was used with a helium flow rate of 85 ml/min and at room temperature. The entire chromatogram of the three components was developed on the recorder chart within a period of approximately four (4) minutes, beginning with the appearance of the nitrogen peak to the end of the CO_2 peak. To reduce the total time necessary for a large number of analyses, the second sample could be injected into the column before the chromatogram of the first sample was developed, as long as the time interval between the injection of the first and second sample exceeded four minutes. In this manner, fifteen routine analyses for N_2, CH_4 and CO_2 could be completed in one hour. A molecular sieve 5A column was used occasionally to analyze separately for O_2, N_2 and H_2.

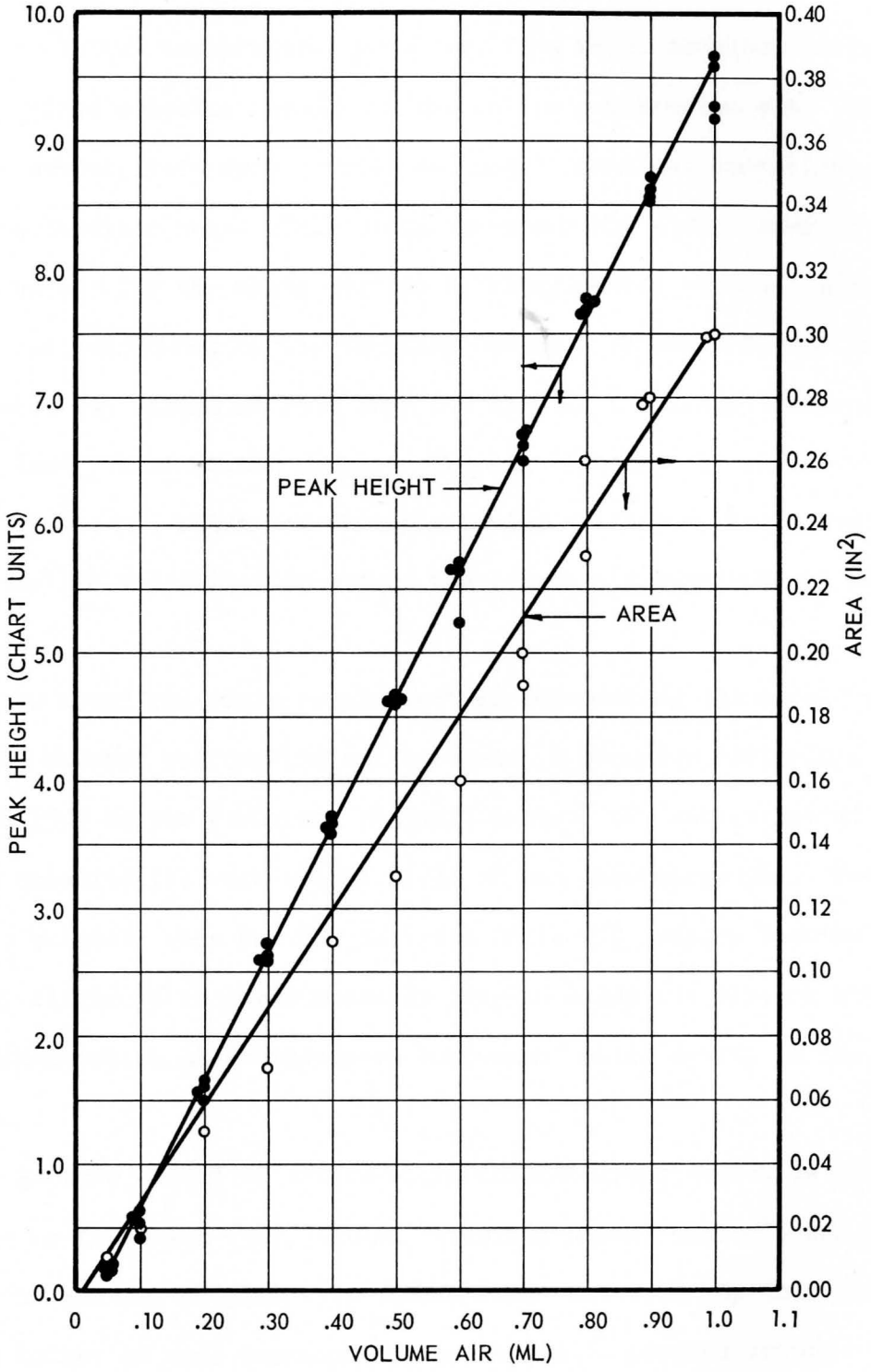
E. Interpretation of Chromatograms

The amount of a gaseous component present in a sample was determined by measuring the area, or the peak height, of its chromatogram. The total area under a series of peaks is directly proportional to the amount of a particular sample present, provided the response of the

detector is linear with respect to the amount of the sample present. The peak height will also be proportional to the amount of sample present if the component peak is symmetrical (55).

The major drawback of the "area-method" is the difficulty to measure the area accurately. As shown by the calibration curves in Figure 10, both the area versus sample volume curve and the peak versus sample volume curve appear as linear relations. The experimental points of the area versus volume relation are more scattered than those of the peak versus sample volume. All areas were carefully measured by a planimeter. A high quality integrator may reduce part of the error of area measurement. However, the reading of an integrator attached to a recorder includes also any shift of the base line, difficult to always maintain exactly at zero. On the other hand, the peak height can be read directly from the recorder chart with a high degree of reproducibility. In practice, it was found that the peak height method is much easier to apply. An accurate quantitative analysis can be obtained by this method even if the chromatogram is asymmetric, provided a carefully prepared calibration curve, although not necessarily linear, is available.

To establish calibration curves various quantities of pure gas samples were injected. Generally, a plot of peak height versus sample size yielded a straight line. By means of calibration curves, peak heights were converted directly to the partial volume of any particular component in the sample. The mole concentration of the component was equal to the partial volume divided by the total sample volume injected. The sample gas was assumed as an ideal solution because of the low pressure and moderate temperature range involved. To obtain reproducible readings, the operating



CALIBRATION CURVES OF PEAK HEIGHT AND AREA VERSUS VOLUME OF AIR SAMPLE

Figure 10.

conditions (column temperature, pressure, flow rate, detector current, etc.) were maintained constant throughout the entire calibration run. Insofar as possible, the analyses were carried out under identical conditions as those for the calibration runs. This requirement was not always easy to achieve and was responsible for the major portion of experimental error. Another source of error was introduced by the sampling device. It was difficult to meter out an exact gas volume of less than 0.2 ml with a syringe because of the inherent dead volume of the needle. The gas-tight microsyringe with a capacity of 0.1 ml, which has recently become available, has a very small dead volume and may assist to reduce the source and magnitude of experimental error.

To avoid the rigid requirement of reproducing identical operating conditions between calibration and analysis, a procedure described by Keulemans (56) as the "internal standard method" or "marker method" is widely used for quantitative work in the field of gas chromatography. However, the method is accurate only for the analysis of liquid samples because it is extremely difficult to experimentally prepare a gaseous mixture with an exact concentration of a "reference component" which serves as the internal standard.

Another method of interpreting chromatograms, which is also described by Keulemans (56), called "internal normalization", has been used in the present studies with considerable success. By this method, the peak height of each component is converted to partial volume by its corresponding calibration curve. The mole fraction of a particular component is equal to its partial volume divided by the summation of the partial volumes of all components emerging from the column. This method

is applicable even if the summation volume, as obtained from the calibration curve, is not equal to the volume of the sample injected, because operating conditions have changed from those under which calibration was carried out. The advantage of the method is that the variation of the experimental conditions, which affect all components equally, will cancel out. Therefore, a moderate deviation of operating conditions, say, one or two degrees change of column temperature or a few milliamperes variation of filament current, will not appreciably affect the resulting analysis. Many of the routine analyses carried out on this project were calculated by the "internal normalization" method.

"Peak Height Fraction" Method:

When gas-liquid partition columns were employed for the analysis of sludge gas, accurate analyses were achieved without the need of calibration curves. It was found that the thermal conductivity is smaller for the CO_2-He mixture than that of the CH_4-He mixture. Consequently, a thermal conductivity cell gave a greater response for CO_2 than for CH_4 with helium as the carrier gas. On the other hand, since CO_2 emerged from the column later than methane, the base of the CO_2 peak was wider than that of CH_4. Because these two factors compensated each other, the peak heights of methane and carbon dioxide were nearly identical for equal size samples. The thermal conductivity of nitrogen or oxygen is almost the same as that of methane, and they emerge from the column only slightly preceding methane. Therefore, the height of a nitrogen or oxygen peak is also nearly the same as a methane peak for samples of equal volume. Air (i.e., nitrogen, oxygen or their mixture), methane and carbon dioxide are the three components usually present in sludge gas. The composition of each component gas was obtained simply by dividing the peak height of each component by the summation of the peak heights of all three components.

To determine the accuracy achieved by the "peak height fraction" method, a 71-ft silicone grease-coated, C-22 firebrick gas-liquid partition column was studied intensively. Several runs were made with samples containing various proportions of CO_2 and CH_4, prepared in a gas mixing chamber[30] based on Dalton's Law of Partial Pressures. From the calibration curve of air, previously obtained (Figure 10), the air fraction present in any sample was determined. The air volume was subtracted from the total volume of sample injected. Based on the known ratio of CO_2 to CH_4, the remaining sample volume was assigned to the two components. The peak height of each component was then plotted against their partial volumes. This plot, as shown in Figure 11, produced an identical straight line for both CH_4 and CO_2 and was found to be very close to the calibration curve of air, as may be observed by comparing the calibration curves in Figure 10 and Figure 11. These calibration curves show that the peak height of chromatograms will be the same for air, CH_4 and CO_2 for equal sample sizes and that the peak response is linear with the sample volume. Therefore, the "peak-height fraction" of any component is equal to the "volume fraction" for the mixtures of air (nitrogen), methane and carbon dioxide.

From the calibration curves obtained previously, it was found that when a thermal conductivity type detector was used, a linear relation generally exists between peak height and volume. Consequently, the ratio of the peak height of CH_4 to CO_2 should be a constant, regardless of the size of sample injected. Any deviation from this constant ratio must be attributed to experimental error. Statistical analyses of the data, obtained from four independent runs with 19 to 33 samples from each

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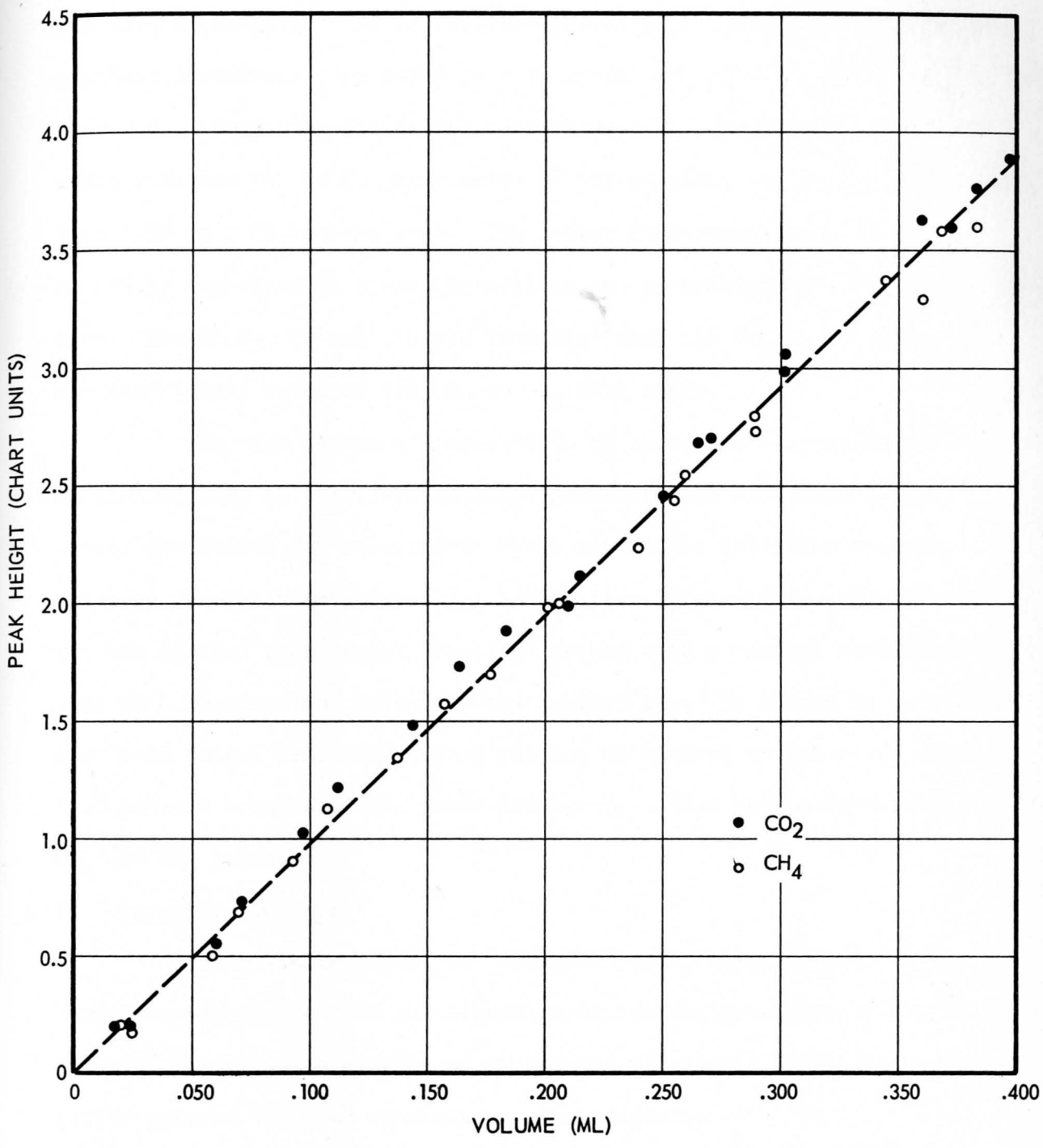
[30] The gas mixing chamber was constructed in this laboratory to prepare standard samples of known composition. For details of this apparatus see Final Report, RG-7001, to N.I.H., pp. 13-16, May 31, 1962.



PEAK HEIGHTS OF CH_4 AND CO_2 VERSUS THEIR PARTIAL VOLUMES IN A SLUDGE GAS SAMPLE

Figure 11.

run used to construct the calibration curves shown in Figure 11, indicated standard deviations from 0.54% to 1.9% of the CH_4 to CO_2 peak ratio from the four runs. Comparing the differences between the average CH_4 to CO_2 peak ratio with the CH_4 to CO_2 mole ratio of the samples, the differences varied from 1.5% to 2.2% between runs. The latter differences included those caused by experimental error, as well as any uncertainty of sample composition. Therefore, it was clearly indicated that the CH_4 to CO_2 peak ratio was essentially equal to the CH_4 to CO_2 mole ratio.

The high degree of correlation of experimental results may be applicable only to the 71-ft silicone grease column discussed above. Larger deviations may result from other gas-liquid partition columns, although generally an accuracy of better than 5% should be expected from the use of the "peak height fraction" method with a thermal conductivity cell as a detector and helium as the carrier gas. It should be noted that the "peak height fraction" method can not be applied to gas-solid adsorption columns because of the great difference of the sharpness between the CH_4 and CO_2 peaks.

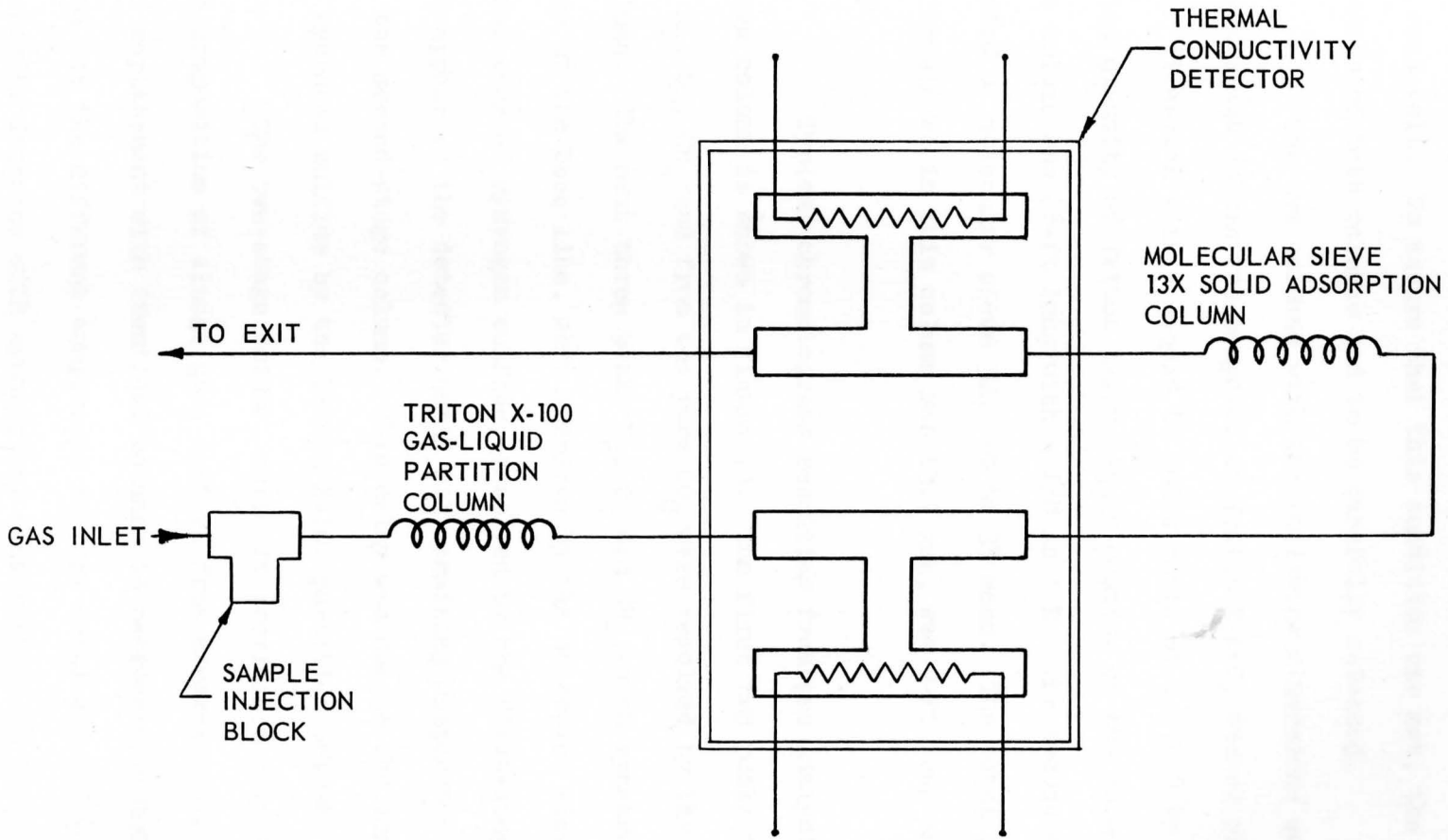
F. Two-Stage Columns

The so-called "air" or "nitrogen" peak, which appears on the chromatograms eluted from gas-liquid partition and gas-solid adsorption columns, represents a mixture of oxygen and nitrogen. It does not necessarily possess the same composition of atmospheric air. In fact, a much higher ratio of nitrogen to oxygen is expected from a sludge digestion gas analysis. The exact amount or the concentration of oxygen in sludge gas may not interest sewage treatment plant personnel during routine operations, but may provide valuable information to research workers.

After a thorough investigation of a wide variety of column materials, it was established that only molecular sieves are capable to resolve oxygen and nitrogen. Unfortunately, this solid adsorbent can not resolve either CO_2 or H_2S, as it adsorbs both components irreversibly. Thus, neither CO_2 nor H_2S will be eluted from this column. To accomplish complete resolution of all components that may be present in ordinary sludge digestion gas, viz., O_2, N_2, CH_4, CO_2 and H_2S, requires two columns in series.

The special chromatographic analysis equipment, developed for this purpose, required only one detector and one recorder for the two-stage column operation. As shown in Figure 12, the sample passed first through a gas-liquid partition column which separated sludge gas into three groups: (1) a mixture composed of oxygen, nitrogen and methane, (2) pure carbon dioxide and (3) pure hydrogen sulfide. These three groups of gases passed through one side of a thermal conductivity detector and were registered on the recorder as three peaks. The gases then entered a molecular sieve column which adsorbed carbon dioxide and hydrogen sulfide irreversibly, while the mixture of nitrogen, oxygen and methane was separated into the individual components. They passed through the other side of the thermal conductivity cell and were recorded as three additional peaks, but in the direction opposite to the previous peaks due to the change of polarity of the output signals.

In this two-stage arrangement, each of the two sides of the thermal conductivity detector served alternately as the reference cell and the sample cell. Therefore, it was important to prevent any sample gas from entering the reference cell side while the sample gases were passing through the other side of the cell for their quantitative measurement, and vice versa. This restriction was necessary because the entire



SCHEMATIC DIAGRAM OF TWO-STAGE COLUMNS ARRANGEMENT

Figure 12.

analysis was based on a comparison of thermal conductivities of the gases in each cell. To assure that this condition was met, the respective lengths of both columns had to be carefully selected.

The two columns with the following dimensions were used: The first-stage column was composed of Triton X-100, coated on 28 to 48 mesh, C-22 firebrick with a liquid to solid ratio of 1 : 2.3 by weight. The total quantity of Triton X-100 liquid coating on the column was 14.16 gms. The column was 26-ft long with a 1/8 in I.D. The second-stage column consisted of molecular sieve 5A, 28 to 35 mesh. The total quantity of molecular sieves in this column was 13.7 gms, was 9-ft long and also of 1/8 in I.D.

Typical chromatograms resulting from gas analysis with the two-stage column is shown in Figure 13. The first two peaks from the mixture of N_2, O_2, CH_4 and from the pure CO_2 were resolved by the Triton X-100 column. The next three peaks N_2, O_2 and CH_4, which appeared on the opposite side of the base line, were resolved by the molecular sieve column. The final peak of hydrogen sulfide, resolved by the first-stage column, did not appear at the detector until all remaining components had been resolved by the second-stage column. This delay was due to the long retention time of hydrogen sulfide by the Triton X-100 partition column.

The two-stage column, while it provides a detailed analysis of the composition of sludge gas, suffers from several rigid requirements: (1) replacement with identical columns is necessary because the elution time for the different components is very critical; (2) a thermal conductivity detector with symmetrical construction of both cell sides is required; (3) frequent renewal of the molecular sieve column is necessary

GAS CHROMATOGRAPHIC ANALYSIS UTILIZING TWO-STAGE COLUMNS

COLUMN I: 26 FT. TRITON X-100 ON C-22 FIREBRICK
COLUMN II: 9 FT. MOLECULAR SIEVE 5A
FLOW RATE: 31 MLS/MIN.
SAMPLE SIZE: 1.0 ML TOTAL
COLUMN TEMPERATURE: 80°F

Figure 13.

because of its relatively short life due to the irreversible adsorption of water vapor, CO_2 and H_2S; and (4) a calibration curve is needed for each gaseous component. The simpler "peak height fraction" method, discussed in Section E, "Interpretation of Chromatograms", is not applicable because it is only valid for gas-liquid partition columns, while in this case a molecular sieve, gas-solid partition column is involved.

Chapter 8

SUMMARY OF RESULTS

A. Criteria for Column Selection

The selection of the proper column is based primarily on (a) the ability to separate the individual components of the gas mixture to be analyzed, and (b) to perform the separation within a reasonable length of time. In a mixture containing several components, the pair of components most difficult to separate usually dictates the choice of the column. In the analysis of sludge digestion gas, N_2 and CH_4 constitute the most difficult pair to be separated. In fact, most workers in the field of gas chromatography still believe that this separation may only be achieved by a gas-solid adsorption column, but a number of gas-liquid partition columns were found to be equally useful, and actually more versatile for sludge digestion gas analysis.

To eliminate trial and error methods and to place the determination of the most appropriate liquid or solid adsorbent for the separation of any pair of components on a rational basis, the specific retention volumes of the components in the partition liquid or solid adsorbent should be established first. The difference of specific retention volumes of the two components determines the degree of separation which may be obtained. The greater this difference, the better the degree of separation to be achieved.

Table IX in Chapter 4 shows that silicone grease and squalane are superior partition liquids for the separation of nitrogen and methane. Another excellent liquid coating material is tetra-iso-butylene, but it

also slightly separates oxygen and nitrogen. Therefore, the air peak is broadened and its height depends on the relative ratio of the oxygen and nitrogen concentrations. The incomplete separation of the air peak complicates the quantitative interpretation of the chromatogram. Silica gel provides too broad and flat a peak for carbon dioxide analysis. Molecular sieves adsorb carbon dioxide irreversibly. Furthermore, the column life of both solid adsorption columns is short because they adsorb water vapor from the atmosphere or carrier gas. Therefore, solid adsorbents are not as desirable as silicone grease or squalane, as column materials for the analysis of sludge digestion gas.

The column of choice between silicone grease and squalane appears to be the former because it provides the longer column life. Silicone grease, primarily used as a high vacuum stopcock lubricant grease, has an extremely low vapor pressure at temperatures below 100°C. A 71-ft column, packed with silicone grease coated firebrick C-22 (ratio of 40 to 100, liquid to solid by weight), operated at a column temperature of 80° to 85°F, was used to analyze 16 to 18 sludge gas samples daily for a period of two years. It separates N_2, CH_4, CO_2 and H_2S, and the column remains in excellent condition.

For the "complete" analysis of sludge digestion gases, including trace components by two-stage columns in series operation, Triton X-100[31] is recommended as the first stage column because it provides the best separation between methane and carbon dioxide and between carbon dioxide and hydrogen sulfide. A column with dimethyl sulfolane gives a greater specific retention volume for carbon dioxide, however, its column life is

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[31] Manufactured by Rohm & Haas, Philadelphia, Penna.

relatively short because of the relatively high volatility. For the second stage column, required to separate oxygen, nitrogen and methane, molecular sieves, type 5A or 13X, are the only choice, because they are the only adsorbents capable of separating oxygen from nitrogen. Among these two, molecular sieve 5A appears to be a better choice because it exhibits the greater resolving power as shown in Table IV.

Upon selection of the appropriate partition liquid and solid adsorbent for the two-stage technique, adequate lengths of columns and optimum operating conditions for the analysis of sludge gas remain to be determined. The separation factor is used in this case as a quantitative parameter to measure the exact degree of separation between two components achieved by a certain column under the specified operating conditions. Again, the separation of the most difficult pair of components dictates the final choice. Table XI in Chapter 5 shows that the separation factor between N_2 and methane has maximum value of 1.02 when a 71-ft silicone grease column is operated at an inlet pressure of 20 psig and a temperature of 86°F. Although an inspection of the separation factor of 1.0 still indicates an incomplete separation between N_2 and CH_4, it is sufficiently large to provide a good degree of accuracy in the quantitative analysis when their respective peak heights are measured and converted to peak heights. A further increase of the column length does not improve the degree of separation. Instead, the column efficiency decreases which is caused by the increase of the pressure drop across the column.

In two-stage column operation, the determination of optimum column length and operating conditions is further complicated by the fact that the lengths of each of the two columns must be selected so that no individual component of sample gas will be present simultaneously in both

sides of the cells of the thermal conductivity detector (see Chapter 7, Section E, "Two-Stage Columns"). The requirement for an adequate value of the separation factor (greater than 1.5) is still valid but it alone does not satisfy all conditions. It was established experimentally that a combination of a 26-ft Triton X-100 column and a 9-ft molecular sieve 5A column provide good separation between oxygen, nitrogen, methane, carbon dioxide and hydrogen sulfide at a column inlet pressure of 50 psig and room temperature.

In summary, the final selection of columns was narrowed down to:

(1) For single stage column analysis (separates N_2, CH_4, CO_2 and H_2S)

Partition liquid: silicone stopcock grease
Support solid: firebrick C-22
Ratio of liquid to solid: 40 to 100 by weight
Support particles size: 28-48 mesh
Column diameter: approximately 1/4 in I.D.
stainless steel or plastic tubing
Column length: 71-ft.

(2) For two-stage column analysis: (separates N_2, O_2, CH_4, CO_2 and H_2S)

Column for the first stage:

Partition liquid: Triton X-100
Support solid: firebrick C-22, 28-48 mesh
Ratio of liquid to solid: 30 to 100 by weight
Column diameter: approximately 1/4 in I.D.
stainless steel or plastic tubing
Column length: 26-ft

Column for the second stage:

Partition liquid: none
Solid adsorbent: Molecular sieve 5A
Particle size: 28-48 mesh
Column diameter: approximately 1/4 in I.D.
stainless steel, copper or plastic tubing
Column length: 9-ft.

B. Interpretation of Gas Analysis Data in Terms of Progress of Sludge Digestion

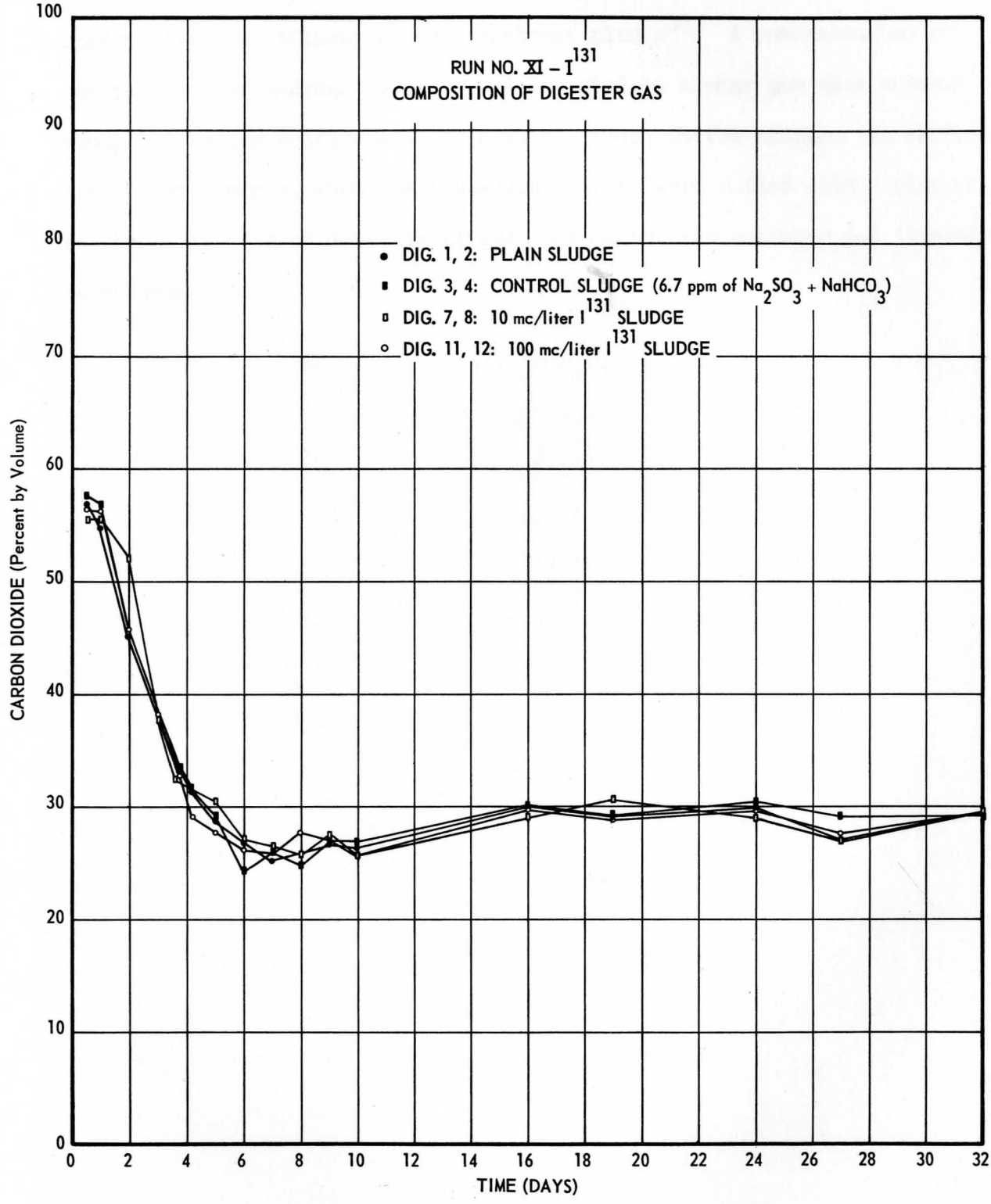
The experimental gas chromatographic analyzer, constructed in this laboratory, was used for the daily analysis of the gases evolved from laboratory sludge digesters. Gas samples from 16 digesters were analyzed daily for the CO_2 to CH_4 ratio. The analyses were performed during 24 experimental digestion studies, ranging from 40 to 90 days each. The relation of the CO_2 to CH_4 ratio to the progress of digestion was observed along with other parameters, such as the rate of gas production, pH, ORP and electric conductivity of the sludge (57)(58).

From the daily gas analyses, the following conclusions may be drawn:

(1) For batch digestion, the initial CO_2 content of the sludge gas generally is 60% (by volume) or higher, but drops down to 20 to 30% after five or six days if digestion proceeds in the normal manner. After ten days of digestion, CO_2 content of sludge gas higher than 30% definitely indicates unfavorable conditions upsetting the normal digestion process (Figure 14). The 30% CO_2 value after ten days of digestion corresponds closely to modern high rate digestion practice and confirms the results obtained in full scale treatment plants.

(2) Nitrogen found in the sludge gas is present either from the atmosphere by leakage into the gas line or from a release of the dissolved gas from the sludge. All experimental evidence points against the theory that any free nitrogen is produced during the decomposition process.

(3) Neither hydrogen sulfide nor hydrogen gas were found in the sludge gas from any of the seeded laboratory digesters containing domestic



CHANGE OF CO_2 CONCENTRATION IN SLUDGE GAS DURING DIGESTION AS MEASURED BY A GAS CHROMATOGRAPHIC ANALYZER

Figure 14.

sludges from two Atlanta sewage treatment plants[32]. A concentration of one per cent of hydrogen sulfide was detected in sludge gas when a small amount of sodium sulfide was deliberately added to the sludge. In another set of experiments, when the digestion bottles were filled with a glucose solution, instead of domestic sludge, 20% of the gas produced was liberated as hydrogen.

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[32] op. cit.

Chapter 9

CONCLUSIONS

1. The analysis of sludge gas was successfully carried out by gas chromatography. It has been demonstrated that gas chromatography is capable of resolving components usually of interest to digester operation, CH_4 and CO_2, on a reliable and routine basis. Gas chromatography is also capable of analyzing for other components which may be present in sludge digestion gas, including H_2S, H_2, N_2 and other trace constituents depending on the needs of the plant operator or as an analytical tool in research.

By the aid of an automatic sampling valve, also developed in this study, sludge digestion gas can be analyzed continuously by gas chromatography to provide complete digestion process information to a plant operator or to an automatic control system.

2. On the basis of extensive investigations, including many different columns, it was found that for routine digestion gas analysis, a 71-ft silicone grease partition column proved to produce the best and most reproducible separation and also least deterioration of column with time. This column can resolve N_2, CH_4, CO_2 and H_2S.

3. Other columns which were also found to be quite satisfactory for sludge digestion gas analysis are: silica gel, tetra-iso-butylene, silicone oil 550, squalane, tri-meta-cresyl phosphate, dimethyl sulfolane, and Triton X-100.

4. For the analysis of specific trace components as may be of interest to research workers, the following columns were found to be of interest:

Gaseous Component	Recommended Column
H_2S	Triton X-100
H_2	Molecular Sieve 5A

5. The resolution of O_2, N_2, as well as other components of sludge digestion gas: CH_4, CO_2 and H_2S, was successfully accomplished by a two-stage column arrangement composed of 9-foot molecular sieve 5A and 26-foot Triton X-100. This type of column arrangement would be most suitable for research studies and probably find exclusive application here, rather than in plant application.

6. Peak heights can be used directly to interpret chromatograms by the "peak height fraction" method when a liquid partition column is used to analyze sludge digestion gas. This method reduces the work of interpretation of analytical data to a minimum for the plant operator.

7. It was found repeatedly from 24 runs, with 16 or more digesters in each laboratory study, that during normal sludge digestion conditions, the CO_2 concentration of the gas was 30% or less by volume. When the CO_2 concentration exceeded 30%, it generally served as a warning signal that the digestion process was upset and a significantly higher concentration indicated that the digester was "stuck".

8. Although the gas chromatographic analysis instrument developed was capable to separate minor components, neither H_2 nor H_2S was found in the seeded sludge mixtures obtained from two domestic sewage treatment plants, receiving a minimum flow of industrial wastes and with relatively short outfall lines.

APPENDIX I

SENSITIVITY OF THERMAL CONDUCTIVITY CELLS

Both hydrogen flame type and argon beta-ray type ionization detectors were investigated but were found to be insensitive to oxygen, nitrogen, carbon dioxide and hydrogen sulfide. As these components include some of the major constitutents of sludge digestion gas, thermal conductivity cells were used exclusively as detectors for the gas chromatographic analysis. Four thermal conductivity cells were employed in these studies: two Gow-Mac filament-type cells, Model NRL; one Gow-Mac filament-type cell, Model 30S; and one Industrial Instruments thermistor-type cell, Model TB S-4S. Their characteristics are listed below:

TABLE XIII

Characteristics of the Thermal Conductivity Detectors

Cell No.	Manufacturer	Model No.	Sensing Elements Type and Number	Dead Volume	Speed (Signal) Response
1	Gow-Mac	NRL	4 tungsten filament wires	2 cc	34 sec
2	Gow-Mac	NRL	4 tungsten filament wires	2 cc	34 sec
3	Gow-Mac	30S	4 tungsten filament wires	4 cc	10 sec
4	Industrial Instruments	TBS-4S	2 glass bead thermistors	1 cc	4 sec

The sensitivities of the detectors may be compared on the basis of the sensitivity index as suggested by Dimbat, et al. (59), which is cited more frequently than any other sensitivity scale in the gas chromatographic literature. When dealing with a gaseous sample, it was found that the original sensitivity index may be modified by expressing the index as a response per unit volume of sample rather than per unit weight of sample. Therefore, the dimension of the sensitivity index becomes millivolt (mv) instead of mv-ml/gm.

The sensitivity index can be calculated simply from the following expression:

$$S' = \frac{AC_1}{VC_2 C_3}$$

where

S' = sensitivity index, mv

A = area under the chromatogram, sq in

C_1 = flow rate of carrier gas ml/min

V = volume of sample, ml

C_2 = recorder sensitivity, inch/mv

C_3 = chart speed, inch/min.

Therefore, sensitivity index has the dimension of millivolt, and it is considered to be independent of the flow rate, volume of the sample gas injected and sensitivity of the recorder chart speed (provided all the variables are linear). The index is a function of the response characteristic of the detectors, as well as the intensity of the filament current, the cell block temperature, the thermal conductivity of the carrier gas and that of the component gas to be detected.

Applying the formulation suggested by Dimbat (59), sensitivity index values obtained for the detection of a number of gases for each of the four cells are shown in Table XIV. These values clearly illustrate the superior sensitivity of the thermistor-type cell.

The thermistor cell is more sensitive to the change of the cell block temperature than the filament cell, as illustrated by the characteristic curve furnished by the manufacturer. This curve indicates a change of output signal from 180 mv to 120 mv when the block temperature increases from 80°F to 100°F, whereas the output of a filament type cell only drops from 60 mv to 50 mv in the same range of temperature change.

TABLE XIV

Sensitivity Index of Various Detectors

Cell No.	Manufacturer	Model	Helium Carrier Gas				
			N_2	CH_4	CO_2	H_2S	NH_3
1	Gow-Mac	NRL	190 (120 ma) (130°F)	160 (120 ma) (130°F)	195 (120 ma) (130°F)	-	-
2	Gow-Mac	NRL	180 (120 ma) (75°F)	170 (120 ma) (75°F)	215 (120 ma) (75°F)	-	94 (120 ma) (75°F)
3	Gow-Mac	30S	193 (130 ma) (80°F)	167 (130 ma) (80°F)	242 (130 ma) (80°F)	205 (130 ma) (80°F)	-
4	Industrial Instruments	TBS-4S	2,400 (13 ma) (110°F)	1,465 (13 ma) (110°F)	2,260 (13 ma) (110°F)	1,331 (13 ma) (110°F)	-

			Nitrogen Carrier Gas		
			H_2	O_2	CH_4
1	Gow-Mac	NRL	284 (110 ma) (75°F)	12 (110 ma) (75°F)	36 (110 ma) (75°F)

APPENDIX II

LIST OF SYMBOLS

A	Area under a chromatogram, sq in
C_1	Volumetric flow rate, ml/min
C_2	Recorder sensitivity, inch/mv
C_3	Chart speed, inch/min
d	Distance between the injection point and the peak of a chromatogram, in, (retention time)
f_c	Pressure correction factor
G	Moles of gas phase in a theoretical plate
$\overline{G}$	Moles of gas phase in a gas chromatographic column, ml
H.E.T.P.	Height equivalent to a theoretical plate, ft
K	Partition coefficient
k	Vapor-liquid equilibrium constant
L	Length of a gas chromatographic column
M_s	Moles of partition liquid or solid adsorbent in each plate
m	Number of moles of gas which have passed plate n
N,n	Number of theoretical plates
P_i	Column inlet pressure, mm.Hg
P_o	Column exit pressure, mm.Hg
R	Separation factor
S	Moles of stationary phase in a theoretical plate
S'	Sensitivity index
$\overline{S}$	Moles of stationary phase in a gas chromatographic column
u	A variable defined by equation (9)

APPENDIX II

LIST OF SYMBOLS
Continued

V_G	Volume of gas in each theoretical plate, ml
V_L	Volume of liquid in each theoretical plate, ml
$\overline{V}_G$	Volume of gaseous phase in a gas chromatographic column, ml
$\overline{V}_L$	Volume of liquid phase in a gas chromatographic column, ml
V_g^o	Specific retention volume, ml/gm
W	Total weight of the liquid phase, gm
w	Peak width
x	Mole fraction of solute in the liquid phase
y	Mole fraction of solute in the vapor phase
θ	Retention time, second
θ_i	Retention time of an inert gas sample, second
ρ	Density of the stationary phase, gm/ml
ρ_G	Density of the gaseous phase, gm mole/ml
ρ_L	Density of the liquid phase, gm mole/ml

Subscripts

1, 2, 3, etc.: Component 1, 2, and 3, etc.

n: Theoretical plate number

APPENDIX III

PROGRESS REPORT AND PUBLICATIONS RESULTING FROM THIS GRANT

Although this is a Final Report of Research Grant RG-4945 entitled "Application of Gas Chromatography to Sludge Digestion Gas Analysis", many interim results and experimental details have already been published in the literature. A list of previous papers and progress reports appears below:

(1) Grune, W.N., Carter, J.V., Jr. and Keenan, J.P., "Development of a Continuous Gas Chromatographic Analyzer for Sludge Digestion Studies", Sewage and Industrial Wastes, 28, 12 1433 (December 1956)

(2) Grune, W.N., Philp, R. H., Jr. and Borsch, R.J., "Applications of O.R.P., Conductivity and Gas Chromatography on Sludge Digestion", presented at 2nd Bio-Oxidation Conference, Manhattan College, New York, 25 April, 1957 (published in Biological Treatment of Sewage and Industrial Wastes, Vol. 2, 80-96, Reinhold Publishing Corporation, New York, 1958)

(3) Grune, W.N., Philp, R.H., Jr. and Cossitt, R.E., "Anaerobic Process Automation by ORP, Conductivity and Gas Chromatography", Proc. 12th Industrial Waste Conference, 14 May 1957, Purdue University, pp. 604-635, May, 1958

(4) Grune, W.N. and Peek, R.C., Jr., "New Parameters for Improving Control of Sludge Digestion", Wastes Engineering, 29, 354, 424 and 468 (1958)

(5) Grune, W.N., Bartholomew, D.D. and Hudson, C.I. Jr., "Effects of Radioactive Materials on Anaerobic Digestion, Part I. Radiophosphorus, and Part II. Radioiodine", Sewage and Industrial Wastes, 30, 1123 (September 1958) and 1399 (November, 1958)

(6) Grune, W.N., Chueh, C.F. and Hawkins, J.M., "Gas Chromatography for Waste Treatment Control", presented at the 32nd Annual Meeting, Federation of Sewage and Industrial Wastes Association, Dallas, Texas, 13 October 1959 (published in Journal, Water Pollution Control Federation, 32, 942-948 (September, 1960))

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(12) Grune, W.N., "Application of Gas Chromatography to Sludge Digestion Gas Analysis", Research Grant No. RG-4945 with the National Institutes of Health, Progress Report Covering the Period from May 15, 1958 to January 31, 1960, Georgia Institute of Technology, Atlanta, Georgia (March 1, 1960)

(13) Grune, W.N. and Chueh, C.F., "Application of Gas Chromatography to Sludge Digestion Gas Analysis", International Journal of Air and Water Pollution, 6, 1962 (in process of publication)

APPENDIX IV

COMPLETE LIST OF PROJECT PERSONNEL

Name	Title	Field of Specialization	Period of Employment
Grune, W.N.	Professor of Sanitary Engineering	Sanitary Engineering	1 Dec 1956-30 May 1962
Chueh, C.F.	Research Assistant	Chemical Engineering	20 Feb 1957-30 May 1962
Philp, R.H.	Research Assistant	Chemistry	1 Jan 1957-28 May 1957
Carter, J.V.	Graduate Research Assistant	Electrical Engineering	1 Dec 1956-30 June 1959
Keenan, J.P.	Research Assistant	Chemical Engineering	1 Dec 1956-30 Jan 1957
Cossitt, R.E.	Student Assistant	Chemical Engineering	1 Dec 1956-15 June 1957
Smith, R.S.	Technical Assistant	Chemistry	20 Jan 1960-4 Apr 1960
Peek, R.C.	Graduate Research Assistant	Chemistry	16 Sept 1957-30 June 1960
Lee, J.G.	Graduate Research Assistant	Electrical Engineering	4 Oct 1957-30 June 1960
Mehaffey, J.H.	Research Assistant	Electrical Engineering	26 Feb 1959-30 May 1962
Horldt, P.C.	Student Assistant	Chemical Engineering	3 Oct 1960-30 June 1961
Keith, Katherine	Secretary		1 Dec 1956-30 May 1962
Dowman, Carolyn	Secretary		1 Oct 1961-30 May 1962

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